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Sulfur in the atmosphere

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8.1. INTRODUCTION

The atmosphere represents an important sulfur reservoir for living organisms. Compared with other sulfur reservoirs such as the oceans or the lithosphere, it acts as a highly mobile medium in which wind distributes sulfate and other essential nutrients over large areas on a relatively short time scale. Biological processes not only make use of atmospheric sulfur, but in turn have a decisive impact on the chemical composition and total burden of sulfur compounds in the atmosphere. Sulfur in various chemical forms is released from many different

organisms as an end-product of their metabolism. In other words, the natural sulfur cycle in our planet's atmosphere is uniquely connected with the geochemical sulfur cycle through the existence and action of life, and in turn through a life-supporting balanced exchange of sulfur between each reservoir. Therefore the presence and fate of sulfur in the atmosphere cannot be understood without knowing its relationship with other sulfur reservoirs, in particular the biosphere. This more holistic view of the atmospheric sulfur cycle as part of the global "biogeochemical" sulfur cycle has now been generally accepted by earth scientists.

Sulfur is one of the major elements essential to life on this planet. Living organisms (including plants) ingest sulfur from their environment, mainly in the form of sulfate or amino acid sulfur. In a process called *assimilatory sulfate reduction*, micro-organisms (bacteria, algae, fungi) and plants use sulfate to build certain proteins to store energy and to support cell growth. During food digestion, energy is released by the decomposition of proteins back into their chemical building blocks, the amino acids. Important sulfur-containing amino acids are cysteine, cystine, and methionine. Their further catabolism results in relatively simple volatile sulfur compounds which the organism releases back into its environment. Animals, including man, are unable to produce sulfur amino acids by this process and thus they depend on plants, fungi, and bacteria as sulfur-supplying food.

Certain micro-organisms living in anoxic environments such as the Earth's crust or the deep oceans obtain energy directly from using sulfate (in place of oxygen) as an electron acceptor. This process is called *dissimilatory sulfate reduction*. The reaction of organic substrate with sulfate during this process can be symbolized by the following equation:

$$2\ CH_2O + SO_4^{2-} = \xrightarrow{\text{multisteps}} 2\ HCO_3^- + H_2S \qquad (8.1)$$

A substantial fraction of the hydrogen sulfide released during this process combines with iron minerals to form pyrite, FeS, and is thus incorporated into the sediment layers of the lithosphere. In general, the turnover of sulfur in dissimilatory processes is several orders of magnitude faster than in assimilatory processes. The biological sulfur cycle is therefore mainly controlled by anaerobic sulfate-reducing bacteria (Thode, 1991). For a more detailed discussion of the biogeochemical mechanisms involved in assimilatory and dissimilatory sulfate reduction the reader is referred to previous reviews given by other authors (e.g., Krouse and McCready, 1979; Andreae and Jaeschke, 1992; and references therein).

An important part of the sulfur cycle in the Earth's crust is microbial decomposition of buried organic matter involving dissimilatory sulfate reduction and the reaction of H_2S with organic matter. This process represents the major

source of sulfur in fossil oil and coal deposits (Orr and White, 1990). Since the beginning of the industrial age, man has been exploiting these fossil deposits as a primary energy source. The combustion of fossil fuels and its expansion on a worldwide scale have led to a dramatic perturbation of the global natural sulfur cycle in the atmosphere. Environmental problems due to anthropogenic sulfur pollution range from local- to global-scale phenomena such as health effects, visibility reduction, acid rain, and global climate change.

Today we know that significant "background" levels of anthropogenic sulfur exist even in the marine atmosphere, e.g., over the North Atlantic, owing to long-range horizontal and vertical mixing processes. However, to this date it still remains a challenging task to assess the potential consequences of global anthropogenic sulfur pollution. Such an evaluation depends to a large extent on our accurate knowledge of the natural, i.e., unperturbed, atmospheric sulfur cycle. Compared with anthropogenic sulfur emissions, current estimates of natural sulfur emissions are more uncertain. Additional sulfur flux measurements are required to reduce these uncertainties.

Furthermore, many aspects of atmospheric sulfur chemistry have yet to be studied. Our understanding of both elementary reaction kinetics and reaction mechanisms involving atmospheric sulfur compounds is crucial to improving current models of the global sulfur cycle as well as parameterizations of important atmospheric processes such as cloud formation and albedo effects in global climate models.

8.2. OVERVIEW OF ATMOSPHERIC SULFUR COMPOUNDS

Four stable isotopes of sulfur are known to occur naturally. Their atomic weight distribution is approximately: 32 (95.0%), 33 (0.76%), 34 (4.22%), and 36 (0.014%), yielding an average value of 32.064. Atmospheric sulfur compounds show small but distinct differences in sulfur isotope ratios, depending on their origin (e.g., burning of coal or oil, sea spray, volcanic emissions, biogenic emissions) and corresponding fractionation processes (Thode, 1991).

Sulfur also occurs in various oxidation states in the atmosphere, mainly as S(−2), S(+4), and S(+6). Compounds containing the highest oxidation state, S(+6), are relatively stable under atmospheric conditions. On the other hand, since the atmosphere is an oxidizing medium, both S(−2) and S(+4) species are subject to reactions with atmospheric oxidants such as O_2, OH, H_2O_2, and O_3. Thus the distribution and residence times of individual S(−2) and S(+4) species in the atmosphere are largely controlled by chemical processes. However, physical processes also play an important role in the atmospheric sulfur cycle. Essentially the cycle begins with the injection of sulfur into the atmosphere and

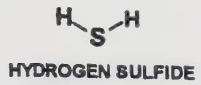
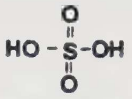
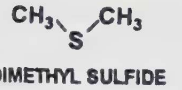
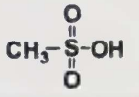
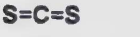
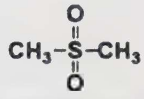
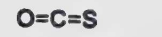
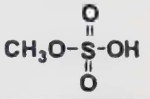
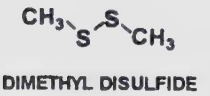
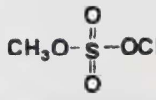
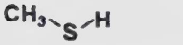
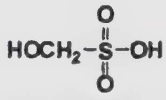
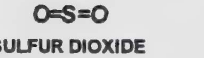
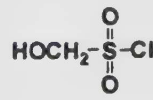
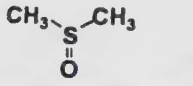
ends with sulfur removal by dry or wet deposition to the Earth's surface. The potential of sulfur compounds to influence physical processes in the atmosphere, such as cloud formation and radiation scattering, increases with oxidation state. This results largely from significant differences in *physical properties* between oxysulfur and reduced sulfur compounds, e.g., corresponding vapor pressures and aqueous solubilities. The following two sections present a short overview of the atmospheric sulfur compounds discussed in this chapter, their physicochemical properties, atmospheric concentrations, and their relationships to important physical processes in the atmosphere.

8.2.1. Physical and Chemical Properties

Table 8.1 presents an overview of the most important sulfur compounds identified to date in polluted and/or relatively clean air. Table 8.2 shows a compilation of basic physical and chemical constants for each compound. Only the free gaseous forms are listed in Table 8.2. With the exception of HMSA, all compounds are known to occur in the atmospheric gaseous phase. Not explicitly included are corresponding ionic species of the same oxidation state occurring in aerosol particles or in the aqueous phase (rain-, fog-, cloud-water, etc.). For example, inorganic sulfates (XSO_4) must be mentioned here as the derivatives of sulfuric acid since they represent a major fraction of the total sulfur mass in the atmosphere. The most important sulfate compounds in the troposphere are ammonium sulfate, $(NH_4)_2SO_4$, and ammonium bisulfate, $(NH_4)HSO_4$, which result from the neutralization or partial neutralization reaction, respectively, between H_2SO_4 and NH_3. Biogenic ammonia emitted mainly from continental environments represents the principal source of free alkalinity in the atmosphere. Compounds formed by aqueous phase absorption and dissociation of gas phase sulfur species are implicitly referred to by the pK values given in Table 8.2.

From a comparison of the Henry law constants in Table 8.2 it follows that the solubility of sulfur compounds increases with oxidation state. Therefore reduced sulfur species occur preferentially in the gas phase whereas the S(+6) compounds are found predominantly in atmospheric (moist) particles or droplets. The extremely low volatility of higher-oxysulfur compounds, in particular H_2SO_4 and MSA, also implies that they have a potential for nucleating new "particles" (low- or subnanometer size range) via self-condensation or binary condensation with water vapor under atmospheric conditions. In general, the chemical reactivity of atmospheric sulfur compounds is inversely related to their sulfur oxidation state. Reduced sulfur compounds are rapidly oxidized by the hydroxyl radical, OH, and to a lesser extent by NO_3 and (possibly) Cl atoms. Their atmospheric lifetimes are typically on the order of a few hours to a few

TABLE 8.1 Currently Identified Atmospheric Sulfur Compounds

Structure and Name	Symbol	Structure and Name	Symbol
 HYDROGEN SULFIDE	(H_2S)	 SULFURIC ACID	(H_2SO_4)
 DIMETHYL SULFIDE	(DMS)	 METHANE SULFONIC ACID	(MSA)
 CARBON DISULFIDE	(CS_2)	 DIMETHYL SULFONE	($DMSO_2$)
 CARBONYL SULFIDE	(OCS)	 MONOMETHYL SULFATE	($MMSO_4$)
 DIMETHYL DISULFIDE	(DMDS)	 DIMETHYL SULFATE	($DMSO_4$)
 METHYL MERCAPTAN	(MeSH)	 HYDROXYMETHANE SULFONIC ACID	(HMSA)
 SULFUR DIOXIDE	(SO_2)	 BIS-HYDROXYMETHYL SULFONE	($BHMSO_2$)
 DIMETHYL SULFOXIDE	(DMSO)		

days. One exception is OCS which has an estimated lifetime of approximately 4 years (Chin, 1992). The residence times of the S(+6) compounds in the troposphere are mainly determined by their physical removal via dry and wet deposition and are typically on the order of a few days. For some organic S(+6)

TABLE 8.2 Physical and Chemical Properties of Atmospheric Sulfur Compounds

Symbol	Mol. Wt.	M.P. (°C)	B.P. (°C)	K_H (25 °C) (mol l^{-1} atm^{-1})		pK_1		pK_2	
Reduced sulfur									
H_2S	34.08	−85.5	−60.7	0.102	[MH]	6.98	[MH]	17.1	[G]
DMS	62.13	−98.3	37.3	0.559	[DW]				
CS_2	76.14	−111.5	46.2	0.044	[AD]	hb			
OCS	60.08	−138.2	−50.2	0.021	[AD]	hb			
DMDS	94.20	−84.7	109.7	0.909	[AD]				
MeSH	48.11	−123.0	6.2	0.394	[AD]	10.70			
Lower oxysulfur									
SO_2	64.07	−72.7	−10	1.42	[M]	1.86	[HUE]	7.20	[SI]
DMSO	78.13	18.4	189	9.74E4	[WB]	32–33	[SJ]		
Higher oxysulfur									
H_2SO_4	98.08	10.4	330	> 1E9	e [RO, A]	−3		1.96	
MSA	96.10	20	167[a]	6.5E13/mH^+	[CB]	−1.86	[CW]		
$DMSO_2$	94.13	110	238	1E5–1E6	e [W]	st	e		
$MMSO_4$	112.10	< −30	130–140 d	< 1E5	e [HE]	dis	[HE]		
$DMSO_4$[b]	126.13	−31.7	188.5 d	< 1E5	e [HE]	hm	[HE]		
HMSA	112.10	?	ust	ug	e [HE]	< 0	[JH]	11.28	[BEH]
$BHMSO_2$	126.13	?	ust	> 1E5	e [HE]	< 0	e	?	

All data from Lide (1991), *CRC Handbook of Chemistry and Physics*, 72 Edn, CRC Press, Boca Raton, FL, and Dean (1992), *Lange's Handbook of Chemistry*, 14th Edn, McGraw Hill, New York, NY, unless specific references are given in brackets. Henry law constants (K_H) refer to physical solubility in pure water. An operational constant is given for MSA [CB] following [BD]; mH^+ is the molal H^+ concentration.
[a]At 10 nmHg. [b]Mutagen and suspected carcinogen. K_H estimated from solubility and/or vapor pressure data given in associated references; e, estimate based on indicated literature; d, decomposes; hb, hydrolyzes to form bisulfide [J, AC]; hm, hydrolyzes to from $MMSO_4$ and H_2SO_4; dis, disproportionates into $DMSO_4$; ug, occurrence in atmospheric gas phase unknown; st, stable; ust, unstable.
[AD] Adewuyi (1989), in *Biogenic Sulfur in the Environment*, Saltzman and Cooper (Eds), *ACS Symp. Ser.*, Vol. 393 p. 529, Am. Chem. Soc., Washington, DC; [AC] Adewuyi and Carmichael (1987), *Environ. Sci. Technol.*, **21**, 170; [A] Ayers et al. (1980), *Geophys. Res. Lett.*, **7**, 433; [BEH] Betterton et al. (1988), *Environ. Sci. Technol.*, **22**, 92; [BD]Brimblecombe and Dawson (1984), *J. Atmos. Chem.*, **2**, 95; [CW] Clark and Woodward (1966), *Trans. Faraday Soc.*, **62**, 2226; [CB] Clegg and Brimblecombe (1985), *Sci. Technol. Lett.*, **6**, 269; [DW] Dacey et al. (1984), *Geophys. Res. Lett.*, **11**, 991; [G] Giggenbach (1971), *Inorg. Chem.*, **10**, 1333; [HE] Hansen and Eatough (1991); [HUE] Huss and Eckert (1977), *J. Phys. Chem.*, **81**, 2268; [JH] Jacob and Hoffmann (1983), *J. Geophys. Res.*, **88**, 6611; [J] Johnson (1981), *Geophys. Res. Lett.*, **8**, 938; [M] Maahs (1983), *J. Geophys. Res.*, **88**, 10721; [MH] Millero and Hershey (1989), in *Biogenic Sulfur in the Environment*, Saltzman and Cooper, Eds, *ACS Symp. Ser.*, Vol. 393, p. 282, Am. Chem. Soc., Washington, DC; [R] Roedel (1979), *J. Aerosol Sci.*, **10**, 375; [SI] Sillen (1964), *Stability Constants of Metal-Ion Complexes. I. Inorganic Ligands*, 2nd Edn, *Chem. Soc. (London) Spec. Publ. 17*; [SJ] Stewart and Jones (1967), *J. Am. Chem. Soc.*, **89**, 5069; [WB] Watts and Brimblecombe (1987), *Environ. Technol. Lett.*, **8**, 483; [W] Watts et al. (1990).

species, such as $MMSO_4$ and $DMSO_4$, photolysis and/or methylation reactions may also be important removal pathways. The latter two compounds are chemically interdependent in the atmosphere and are important to mention because $DMSO_4$ is a known mutagen and suspected carcinogen (Hansen and Eatough, 1991).

8.2.2. Atmospheric Mixing Ratios

Table 8.3 presents measured atmospheric mixing ratios, in parts per trillion by volume (ppt), of the most important sulfur gases in the marine and remote continental atmosphere. This list may not be complete. We believe, however, that the data provide a representative up-to-date view of geographical distributions and trends of the individual sulfur gases in the corresponding regions. These trends and the distributions of other sulfur compounds not listed in Table 8.3 are summarized in the following text.

8.2.2.1. Reduced Sulfur Compounds

DMS

To our present knowledge the major sources and sinks of atmospheric DMS are assimilatory sulfate reduction and photochemical oxidation by OH, respectively. It is now well established that DMS is the dominant sulfur compound emitted from the world's oceans. A precursor of marine DMS is believed to be dimethylsulfonium propionate (DMSP) which is formed and released by certain phytoplankton species (e.g., *Phaeocystis pouchetii*) and bacteria. Aerobic organic soils and certain land plants (e.g., corn, alfalfa, wheat, and the major salt marsh plant *Spartina Alterniflora*) are significant terrestrial sources of DMS.

Following the early studies by Lovelock et al. (1972), numerous measurements of DMS have been conducted in the marine atmosphere and in seawater. Based on these measurements, the DMS mixing ratio in the marine boundary layer (MBL) varies from < 10 ppt in polluted air to 50–100 ppt over oligotrophic waters and up to about 1 ppb over eutrophic (e.g., coastal, upwelling) waters. The global average DMS mixing ratio at sea surface level is approximately 100 ppt. Typically, DMS mixing ratios decline rapidly with altitude to a few ppt in the free troposphere (FT). However, occasionally significant amounts of DMS are "pumped" into the FT by convective clouds and large-scale storm systems such as hurricanes. The latter occur with an average frequency of about 50 year^{-1} and can last for many days. The diurnal cycle of DMS in the MBL strongly depends on photochemical reactions, air mass origin, MBL height, and DMS emission rates. DMS levels with average night/day ratios between 1.0 (no variation) and 3.7 have been reported. The seasonal variation in DMS roughly follows the primary productivity cycle in the oceans. In temperate and high latitudes, spring and summer DMS mixing ratios are typically one order of magnitude higher than in winter.

In continental environments a number of DMS flux measurements have been conducted. However, relatively few atmospheric mixing ratios have been reported. Typical continental surface DMS levels are on the order of 20 ppt or less in rural areas and forests but can reach high ppt levels over wetlands and downwind from industrial sources such as Kraft pulp and paper mills. Recently

TABLE 8.3 Observed Mixing Ratios of Atmospheric Sulfur Gases (ppt)

Location	Range	Average[a]	Remarks	Reference(s)
Dimethylsulfide				
A. Marine surface layer[b]				
Atlantic Ocean	<1–980	80	≤100 ppt: MC and/or OW; R = 1.0–3.7 >100 ppt: MM and/or EW; R = 1.4–2.3 Peak spring/winter ratio: 112 (North Sea)	1–11
Pacific Ocean	5–670	110	5–400 ppt: MM, North Pacific; $R \approx$ 1.0–1.6 <20–670 ppt: MM, South Pacific	1, 12–17, & 74–76
Indian Ocean (Amsterdam I.)	13–400	108	MM; $R \approx 1.6$ Summer/winter ratio: 4–23	18–20
Southern Ocean (south of 40° S)	2–1048	100	MM, EW, and OW; R = 1.4–1.6 (fall, summer) Summer/winter ratio: 10–20 (Cape Grim)	1, 21–24
B. Continental surface layer				
Tropical forests (Amazon, Congo)	5–75	20	No difference between dry and wet seasons; $R \leq 2$ (mainly due to mixing)	25–27
Temperate forests	<1–20	8	Pine forest and rural areas; $R \approx 2.5$	4,28
and rural areas	<10–400	45	Wheat field, spring and summer; $R \approx 3.9$	29
Wetlands,	<1–500	60	Coastal wetlands, marshes	30, 31
temperate NH	4–140	45	Swamps, moors	4, 31
City, industry	440–560	500	Downwind from paper mills (10–70 km)	31, 32
C. Free troposphere (2–5 km)				
Marine (Atlantic,	<1–3	1.5	Relatively stratified atmosphere	2–4, 6, 12
Pacific, S. Ocean)	5–19	15	Strong convection and/or DMS emissions	& 17, 22, 74
Tropical forests	<1–5	1.5		25–27
Germany/Bavaria	<0.1	<0.1		4
Hydrogen sulfide				
A. Marine surface layer[b]				
Atlantic Ocean	<2.5–75	7.5	MM, R = 1.4–1.7, North Atlantic	5, 6, 33
Coastal waters	10–260	65	Mainly advection from coastal wetlands	5, 6, 33
Pacific Ocean	<0.4–14	3.6	MM, no diel trend, equatorial Pacific	34, 75

B. Continental surface layer				
Tropical forests	10–60	35	Amazon, Congo; max. day/night ratio: 4–8	25–27
	105–6400	780/3750	Ivory Coast; above oxic/anoxic soils	35
Temperate forests	5–150	60	Pine forests and rural areas	35–37
and rural areas	< 10–350	100	Wheat field, spring and summer	29
Wetlands, NH	< 3–2740	840	Coastal wetlands, marshes	31, 37, 38
	80–820 +	450	Swamps, moors	4, 31, 37, 38
City, industry	80–810 +	365		38–41
C. Free troposphere (2–5 km)				
Tropical forests	7–13	8.5	Amazon, Congo	26, 27
	70		Ivory Coast	35
Rural areas, NH	1–7	6	France, Germany/Bavaria	4, 35
	140		Advection from coastal wetland areas	4
Carbon disulfide				
A. Marine surface layer[b]				
Atlantic Ocean	1–15	2	Marine air	4, 5, 7, 9, 42
	5–30	18	MM, with continental background air	4, 7, 42
	4–420	150	MC, advection from pollution sources	4, 42
Pacific Ocean	< 6		Marine air	43
	> 20		Advection of pulluted air	43
Southern Ocean	< 7–35 +	< 7	MM, > 7 ppt only in polluted air	24
B. Continental surface layer				
Temperate forest	5–106	35	Pine forest and rural areas	4, 28, 44–46
and rural areas	15–560	80	Wheat field, spring and summer	29
Wetlands, NH	5–390	120	Coastal wetlands, marshes	31
City, industry	65–370	190		44, 47
C. Free troposphere (2–5 km)				
Atlantic Ocean	1–8	5	MM, North Sea; polluted air: ≈ 30 ppt	4
	65–166	115	At 6.1 km, possibly continental air	48
Pacific Ocean	< 6		Marine air	43
Coastal waters	1–21	5.7	At 6 km, MM, mainly SE Pacific coast	49
Continental	< 3–18	7	Continental background air	4, 49, 50

TABLE 8.3 (*Continued*)

Location	Range	Average[a]	Remarks	Reference(s)
Carbonyl sulfide				
Total troposphere				
Northern hemisphere	300–1800	512 + 119	All data (n = 1066), incl. pollution	51
10° N–85° N, 52° E–155° W		514 ± 64	Flight data only (n = 464), no trends	51 (& 4, 7, 43, 48)
Arizona and Swiss Alps		530 ± 40	No trend over last decade	52
A. Marine surface layer[b] (All oceans)	400–800	500	Advection of continental air: > 600 ppt North Sea: 740 ppt (0.2 km)	4, 7, 24, 43, & 53–56
B. Continental surface	300–1800	545	Max. values in polluted air and wetlands	
	500–7000		Wheat field, summer	29
Tropopause and stratosphere	280–520	380	At 10–15 km, declines with altitude	46, 57, 58
	< 10–30	16	At 27–31 km	57–59
Sulfur dioxide[c]				
Total troposphere				
Pacific and Western	MBL: 54 ± 19,	FT: 85 ± 28	Marine atmosphere	60
N. America (57° S–70° N)	MBL: 112 ± 79,	FT: 160 ± 100	Continental atmosphere	
Coastal Europe/N. &	20–1100	260 ± 257	At 0–4 km, decrease to 4 km; max.: 35° N–65° N	61
S. America/Africa/Atlantic	20–300	120 ± 84	At 4–10 km, increase to 7 km, then decrease	
65° N–60° S, 80° W–15° E	48–138	78 ± 31	Lower stratosphere; higher than below tropopause	
A. Surface layer (All oceans)	< 4–160	20	Marine air; summer/winter ratio: 6–9 at Amsterdam I. (Indian Ocean)	12, 20–22, & 60–65, 74–76
Spitsbergen (1983–1992)	14–1880	210	Monthly averages, winter/summer ratio: 10	66
Atlantic, E. Pacific	9–770	130	Near coasts, mixed marine/continental air	8, 13, 16
Atlantic, E. Pacific	150–6000	1500	MC, polluted air	8, 67–69
Amazon forest	10–50	25	Up to 1 km, without biomass burning	25, 26
Rural areas, NH	80 7000	~2000	Varies *strongly* with air mass	28, 31, 70

B. Free troposphere (2–5 km)				
North Pacific	10–300	≥20	Air masses from Asia and/or Mt Pinatubo	12, 64
Southern Ocean	12–20	16 ± 3	Marine air; South Pacific: 10–80 ppt	22
Amazon forest		17	Wet and dry season	25, 26
C. Upper FT (> 5 km)/lower stratosphere				
Europe, North Sea, and Arctic	10–400	50	Refs 70–72: constant profile Ref. 73: strong decrease to 10 ppt	46, 70–73

Data with potentially significant bias due to use of inadequate oxidant scrubbers (DMS data) or interference by OCS (H_2S data) are not included in this table. Surface layer data include measurements up to *ca* 300 m altitude.

[a]Weighed by number and spatial coverage of data. [b]Coastal wetlands not included. [c]Remote regions only. MBL, marine boundary layer; FT, free troposphere; NH, northern hemisphere; EW, eutrophic waters; OW, oligotrophic waters; *R*, average night-time maximum/daytime minimum ratio; MM, mainly marine air; MC, mainly continental air. 1 Andreae et al. (1985), *J. Geophys. Res.*, **90**, 12,891; 2 Ferek et al. (1986), *Nature*, **320**, 514; 3 Van Valin et al. (1987), *Geophys. Res. Lett.*, **14**, 715; 4 Georgii et al. (1987), *Ber. Inst. Meterol. Geophys.*, **68**, Univ. Frankfurt; 5 Saltzman and Cooper (1988), *J. Atmos. Chem.*, **7**, 191; 6 Andreae et al. (1990), *EOS*, **71**, 1254; 7 Bates and Johnson, (1990), *EOS*, **71**, 1255; 8 Berresheim et al. (1991), *Tellus B*, **43**, 353; 9 Cooper and Saltzman (1991), *J. Atmos. Chem.*, **12**, 153; 10 Bürgermeister and Georgii (1991), *Atmos. Environ.*, **25A**, 587; 11 Davison and Hewitt (1992), *J. Geophys. Res.*, **97**, 2475; 12 Andreae et al. (1988), *J. Atmos. Chem.*, **6**, 149; 13 Bates et al. (1990), *J. Atmos. Chem.*, **10**, 59; 14 Quinn et al. (1990), *J. Geophys. Res.*, **95**, 16,405; 15 Bandy et al. (1992), *EOS*, **73**, 28; 16 Bates et al. (1992), *J. Geophys. Res.*, **97**, 9859; 17 Berresheim et al. (1993), *J. Geophys. Res.*, **98**, 12,701; 18 Nguyen et al. (1990), *J. Atmos. Chem.*, **11**, 123; 19 Nguyen et al. (1992), *J. Atmos. Chem.*, **15**, 39; 20 Putaud et al. (1992); *J. Atmos. Chem.*, **15**, 117; 21 Berresheim (1987), *J. Geophys. Res.*, **92**, 13,245; 22 Berresheim et al. (1990), *J. Atmos. Chem.*, **10**, 341; 23 Ayers et al. (1991), *Nature*, **349**, 404; 24 Staubes and Georgii (1993), *Tellus B*, **45**, 127; 25 Andreae and Andreae (1988), *J. Geophys. Res.*, **93**, 1487; 26 Andreae et al. (1990), *J. Geophys. Res.*, **95**, 16,813; 27 Bingemer et al. (1992), *J. Geophys. Res.*, **97**, 6207; 28 Berresheim and Vulcan (1992), *Atmos. Environ.*, **26A**, 2031; 29 Hofmann et al. (1992), in *Precipitation Scavenging and Atmosphere–Surface Exchange*, Schwartz and Slinn, Eds, Hemisphere, Washington, DC, p. 967; 30 Maroulis and Bandy (1977), *Science*, **196**, 647; 31 Berresheim (1993), *Atmos. Environ.*, **27A**, 211; 32 Bürgermeister (1984), *M.S. Thesis*, Univ. Frankfurt; 33 Andreae et al. (1991), *J. Geophys. Res.*, **96**, 18,753; 34 Yvon et al. (1993), *J. Geophys. Res.*, **98**, 16,979; 35 Delmas et al. (1980), *J. Geophys. Res.*, **85**, 4468; 36 Natusch et al. (1972), *Anal. Chem.*, **44**, 2067; 37 Jaeschke et al. (1978), *Pure Appl. Geophys.*, **116**, 463; 38 Jaeschke and Herrmann (1981), *Int. J. Environ. Anal. Chem.*, **10**, 107; 39 Jaeschke et al. (1980), *J. Geophys. Res.*, **85**, 5639; 40 Breeding et al. (1973), *J. Geophys. Res.*, **78**, 7057; 41 Slatt et al. (1978), *Atmos. Environ.*, **12**, 981; 42 Kim and Andreae (1987), *J. Geophys. Res.*, **92**, 14,733 43 Blomquist et al. (1992), *EOS*, **73**, 27; 44 Maroulis and Bandy (1980), *Geophys. Res. Lett.*, **7**, 681; 45 Jones et al. (1983), *J. Atmos. Chem.*, **1**, 65; 46 Griffith and Schuster, (1987), *J. Atmos. Chem.*, **5**, 59; 47 Sandalls and Penkett (1977), *Atmos. Environ.*, **11**, 197; 48 Carroll (1985), *J. Geophys. Res.*, **90**, 10,483; 49 Tucker et al. (1985), *Geophys. Res. Lett.*, **12**, 9; 50 Bandy et al. (1981), *Geophys. Res. Lett.*, **8**, 1180; 51 Bandy et al. (1992), *J. Atmos. Chem.*, **14**, 527; 52 Rinsland et al. (1992), *J. Geophys. Res.*, **97**, 5995; 53 Rasmussen et al. (1982), *Atmos Environ.*, **16**, 1591; 54 Johnson and Harrison (1986), *J. Geophys. Res.*, **91**, 7883; 55 Bingemer et al. (1990), *J. Geophys. Res.*, **95**, 20617; 56 Mihalopoulos et al. (1991), *J. Atmos. Chem.*, **13**, 73; 57 Inn et al. (1979), *Geophys. Res. Lett.*, **6**, 191; 58 Leifer (1989), *J. Geophys. Res.*, **94**, 5173; 59 Zander et al. (1988), *J. Geophys. Res.*, **93**, 1669; 60 Maroulis et al. (1980), *J. Geophys. Res.*, **85**, 7345; 61 Ockelmann (1988), *Ber. Inst. Met. Geophys.*, **75**, Univ. Frankfurt; 62 Herrmann and Jaeschke (1984), *J. Atmos. Chem.*, **1**, 111; 63 Pszenny et al. (1989), *J. Geophys. Res.*, **94**, 9818; 64 Thornton et al. (1992), *EOS*, **73**, 28; 65 Saltzman et al. (1993), *J. Atmos. Chem.*, **17**, 73; 66 H. Dovland and E. Joranger (1993), personal communication; 67 Thornton et al. (1987), *Global Biogeochem. Cycles*, **1**, 317; 68 Saltzman et al. (1986), *J. Geophys. Res.*, **91**, 7913; 69 Luria et al. (1987), *Atmos. Environ.*, **21**, 1631; 70 Georgii and Meixner (1980), *J. Geophys. Res.*, **85**, 7433; 71 Jaeschke et al. (1976), *Geophys. Res. Lett.*, **9**, 517; 72 Meixner (1984), *J. Atmos. Chem.*, **2**, 175; 73 Möhler and Arnold (1992), *Geophys. Res. Lett.*, **19**, 1763; 74 Thornton and Bandy (1993), *J. Atmos. Chem.*, **17**, 1; 75 Yvon et al. (1992), *EOS*, **73**, 81; 76 Huebert et al. (1993), *J. Geophys. Res.*, **98**, 16,985.

DMS levels up to 1 ppb have also been measured in an African rain forest as a result of high DMS emissions from certain tree species (J. Kesselmeier, 1993, personal communication).

H_2S

As discussed earlier, H_2S is the dominant end-product of dissimilatory sulfate reduction. It is rapidly oxidized in the atmosphere by OH. Although marine sediments are a major source of H_2S, very little escapes into the atmosphere (from the open ocean) due to its oxidation in aerobic surface waters. On a global scale H_2S is mainly emitted from terrestrial sources such as anoxic soils, tidal flats, plants, and various industrial sources (e.g., paper and cellulose industry). It is also the dominant reduced sulfur gas emitted by volcanoes.

Average surface-level H_2S mixing ratios over remote oceans are 5–15 ppt and show approximately 1.5 times higher values at night than during daytime. Values ranging between 100 and 300 ppt have been measured over shallow coastal waters, while values up to 1 ppb, with large spatial and temporal fluctuations, have been observed over tidal flats, coastal wetlands, and swamps. In temperate latitudes H_2S levels range between 5 and 150 ppt over vegetated and non-vegetated soils. Relatively moderate H_2S mixing ratios (30–40 ppt at ground level, 1–10 ppt at 3 km) have been measured in and above tropical forests, with the exception of very high levels observed in an Ivory Coast forest (Table 8.3, reference 35). H_2S mixing ratios up to 1 ppb and up to 100 ppb have been measured downwind from industrial sources and in volcanic plumes, respectively.

OCS

Due to its low chemical reactivity, OCS is the most abundant sulfur gas in the global background atmosphere. It is also the only sulfur gas (except during large volcanic eruptions) which can diffuse into the stratosphere where it can be photolyzed at < 388 nm (energetic threshold). Major tropospheric sinks for OCS appear to be uptake by plants and hydrolysis in natural waters.

Measurements of atmospheric OCS and CS_2 mixing ratios and fluxes have been reviewed in detail by Chin and Davis (1993). OCS shows an average tropospheric mixing ratio of approximately 500 ± 50 ppt and no significant variation with altitude up to about 15 km. In the stratosphere it declines rapidly to levels of 10–20 ppt between 25 and 35 km. Long-term measurements over remote marine and continental regions have shown no statistically significant seasonal or secular trends of OCS. However, individual measurements over the Atlantic Ocean have shown elevated OCS levels (up to 800 ppt) in the northern hemisphere, indicating a possible impact of anthropogenic sources on global atmospheric OCS levels.

Other Reduced Sulfur Species

CS_2 is the major chemical precursor for OCS in the atmosphere. Its mixing ratio in the lower troposphere varies from less than 10 ppt over open ocean areas to 15–50 ppt in background continental air and several hundred ppt in polluted air. Most airborne studies have shown a strong decrease in CS_2 levels with altitude (typically 5–7 ppt at 2–5 km in background air) but relatively high levels (up to 166 ppt at 6 km) have also been observed. DMDS and MeSH are probably only important in the vicinity of specific industrial sources such as Kraft pulp mills and refineries. Atmospheric mixing ratios of MeSH over the surface ocean and in tropical forests are typically < 5 ppt.

8.2.2.2. Oxysulfur Compounds

SO_2

Sulfur dioxide is the most abundant anthropogenic sulfur pollutant. It is predominantly emitted through fossil fuel combustion and is also a major product of the oxidation of reduced sulfur compounds in the atmosphere. Boundary layer SO_2 mixing ratios in continental background air range from about 20 ppt to 1 ppb. They can reach tens of ppm in power plant and volcanic plumes. In the marine boundary layer downwind from anthropogenic sources, SO_2 levels can still be as high as a few ppb. Due to its solubility (Table 8.2) and high reactivity in the aqueous phase, atmospheric SO_2 can be rapidly removed by absorption and oxidation in cloud and fog droplets ("rain-out") or during precipitation events ("wash-out").

Average SO_2 values measured in relatively unpolluted MBL air range between 20 and 50 ppt. Airborne studies by Maroulis and co-workers in the marine atmosphere revealed an increase in SO_2 levels from approximately 50 ppt in the MBL to 85 ppt in the free troposphere. Earlier aircraft measurements by Meixner, Jaeschke, Georgii, and others over continental areas showed a vertical decrease in SO_2 levels to about 30–70 ppt at 6 km and no further decline up to and above the tropopause at approximately 12 km (Warneck, 1988). Recent measurements over the Arctic (Table 8.3) reveal yet another vertical trend, with SO_2 levels slightly decreasing up to the tropopause and rapidly decreasing in the lower stratosphere.

H_2SO_4, MSA, and Their Aerosol and Aqueous Phase Ions

Gaseous sulfuric acid in the atmosphere is mainly a product of the reactions of SO_2 with OH and of SO_3 with water vapor. The only known precursor of gaseous methanesulfonic acid, MSA(g), in the atmosphere is DMS. Since both H_2SO_4 and MSA(g) rapidly condense and/or interact with particles in the atmosphere, their vapor mixing ratios are very low in background air. A mass spectrometric detection technique for both gases has only recently been developed (Eisele and Tanner, 1993). It is based on atmospheric pressure, selected ion chemical

ionization mass spectrometry (SI/CI/MS), and offers a real-time detection sensitivity of 10^{-3} ppt. Initial field measurements with this technique (Berresheim et al., 1993a; Eisele and Tanner, 1993) have shown a strong diurnal variation in both gases basically tracking the solar radiation flux. H_2SO_4 levels in rural continental and marine air ranged from a few ppq (parts per quadrillion) at night to 1.2 ppt at midday. A relatively smaller range, under mostly cloudy conditions, was observed for MSA(g) in marine air (0.002–0.2 ppt).

In contrast with the above-mentioned measurements in the gas phase, numerous measurements of sulfate and methanesulfonate, MSA(p), in atmospheric particles and droplets have been made by various investigators. Anthropogenic sulfate pollution and the distribution of continental sulfate in the atmosphere are discussed in detail in Chapters 4, 5, and 12. Aerosol sulfate mixing ratios typically range from less than 200 ppt over remote continental areas to about 1–2 ppb in rural areas and $\geq$2 ppb (24 h average) in polluted air. (For aerosol compounds we define mixing ratios in moles of substance/mole of air; e.g., 1 ppt = 10^{-12} mole/mole; 22.4 ppt = 1 nmol m^{-3} at STP.) Aqueous phase concentrations over the continents are typically 10–50 μM in rainwater, 20–100 μM in cloudwater, and several hundred μM in fogwater (e.g., NAPAP, 1991).

Generally, less than half of the sulfate mass in the marine atmosphere derives from sea water sulfate. Other sources such as reduced sulfur oxidation, advection of soil dust, and anthropogenic sulfate contribute about 50–80%. The concentration of this so-called non-sea-salt sulfate, nss-SO_4^{2-}, is usually calculated from the total sulfate and sodium content of the aerosol:

$$[\text{nss-}SO_4^{2-}] = [SO_4^{2-}(\text{total})] - 0.0603\ [Na^+] \tag{8.2}$$

The brackets in equation (8.2) represent mol m^{-3} units and the factor on the right-hand side represents the average $[SO_4^{2-}]/[Na^+]$ mole ratio in seawater, which is assumed to be constant. Levels of nss-SO_4^{2-} in the remote MBL vary from about 5–50 ppt over the Southern Ocean to 50–200 ppt over most of the Pacific to 100–700 ppt over the northern central Atlantic. In the northern hemisphere significant enhancements of nss-SO_4^{2-} levels in both the MBL and FT have been observed as a result of long-range transport of continental air. A continental influence appears to be negligible over most of the remote Southern Ocean where nearly constant vertical profiles of nss-SO_4^{2-} have been measured. Seasonal variations observed in the MBL over the Pacific and northern Atlantic show a maximum in fall and a minimum in spring (amplitude ratio 1.6–1.7) (Savoie and Prospero, 1989). A much larger seasonal variation (factor of 5–10; 7 ppt in mid-winter, 50 ppt in mid-summer) has been recorded at Cape Grim, Tasmania (40° S) (Ayers et al., 1991). However, with respect to all the data reported it must be kept in mind that calculations of nss-SO_4^{2-} levels based on equation (8.2) frequently

involve the subtraction of two large numbers (i.e., total SO_4^{2-} minus sea salt SO_4^{2-}) leading to high uncertainties in nss-SO_4^{2-} values.

MSA(p) mixing ratios are mainly determined by the distribution of DMS emission sources and by deposition processes. Values of < 10 ppt and 5–100 ppt have been measured in rural and urban air, respectively. MSA(p) levels in the MBL are on the order of 5–15 ppt, with maximum values occurring at high latitudes. The vertical distribution of aerosol MSA(p) typically shows values of ≤ 5 ppt at 3 km in the marine FT. Aqueous MSA(p) concentrations have also been measured in marine cloudwater, with values ranging between 0.2 and 5.2 μM (Table 8.3, reference 22). The seasonal cycle of MSA(p) in the MBL appears to increase with latitude. Summer/winter ratios of 12–25 and higher have been reported for latitudes $\geq 40°$ in both hemispheres. A similar variation has also been observed for MSA(p) in rainwater at Cape Grim (1.0–1.6 μM in summer, 0.1 μM in winter).

DMSO and $DMSO_2$

Dimethylsulfone and its precursor, dimethylsulfoxide, are potentially important oxidation products of DMS. Measurements of both gases in ambient air were first conducted by Harvey and Lang (1986) using an off-line preconcentration-sampling technique (typical sample integration time 8–12 h). For both gases values between 0.6 and 1.6 ppt were found in coastal Miami air. More recent measurements over the North Atlantic (Pszenny et al., 1990) showed a much larger range of mixing ratios for DMSO (< 0.7–271 ppt) and $DMSO_2$ (< 0.7–56 ppt). The relatively long sampling times required make the above technique unsuitable for mechanistic studies of DMS chemistry in the atmosphere. Recently, a real-time SI/CI/MS method has been developed for DMSO with a detection limit of 0.5 ppt at a statistical signal integration time of 60 s (Berresheim et al., 1993b). First measurements with this technique have been conducted at an elevated coastal site in Washington state (Berresheim et al., 1993a). DMSO showed a significant diurnal variation ranging from < 0.5 ppt at night to 3.2 ppt during daytime. The potential implications of these measurements for our understanding of atmospheric DMS chemistry will be discussed in Section 8.3.2.1.

Liquid-based techniques have been used to measure DMSO and $DMSO_2$ in rainwater and aerosol. Coastal rainwater samples showed DMSO concentrations between < 0.1 and 100 nM (Harvey and Lang, 1986). Both compounds have also been measured in marine aerosol (Watts et al., 1990), showing summer maxima of 0.1 and 0.03 ppt, respectively. Winter minima were about 30–50 times lower.

Other Oxysulfur Compounds

HMSA is formed in atmospheric hydrosols via addition of formaldehyde to bisulfite. It largely resists oxidation by dissolved O_3 and H_2O_2. Direct

measurements of HMSA in urban fog samples have shown concentrations of 0–140 μM (Munger et al., 1986). Other studies have inferred HMSA concentrations from measuring the difference between the total S(+4) and "free" sulfite/bisulfite content in hydrosols (e.g., Chapman, 1986). Total S(+4) levels in marine stratus clouds and in precipitation were typically $\leq 10\,\mu M$, but values up to 3 mM have been measured in urban fog. The results indicate that HMSA and possibly other aldehyde–bisulfite adducts may represent a substantial or sometimes even dominant fraction of S(+4) in the atmospheric aqueous phase.

Measurements and the atmospheric chemistry of $MMSO_4$, $DMSO_4$, and $BHMSO_2$ have recently been reviewed by Hansen and Eatough (1991). The former two compounds occur predominantly in the gas phase. They are most likely formed from the reaction of methanol with sulfuric acid in the atmosphere. Mixing ratios between 45 and 450 ppt have been measured in urban air and may reach levels two to five times higher than SO_2 downwind from power plant emissions. $BHMSO_2$ has only been found in aerosol particles, typically at 40–350 ppt in urban air. However, under conditions favorable for its production, concentrations may range up to one order of magnitude higher than those of aerosol sulfate. A mechanism proposed by Hansen and Eatough (1991) for $BHMSO_2$ formation in the atmosphere involves reactions of ethene, ozone, and SO_2.

8.3. THE ATMOSPHERIC SULFUR CYCLE

An overview of the most important processes involved in the atmospheric sulfur cycle is given in Figure 8.1. In addition, other more temporary phenomena can also be of importance on both regional and global scales. Noteworthy among these are biomass burning and rapid vertical mixing of air in connection with cumulonimbus clouds or large storm systems such as hurricanes.

Anthropogenic sources emit predominantly SO_2 into the atmosphere. The major sulfur gases released by natural sources are DMS, H_2S, OCS, and CS_2. Only volcanism emits significant amounts of natural SO_2 into the air. Most of the sulfate mass injected through sea spray, soil erosion by wind, volcanism, or industrial activities is concentrated in relatively large micron-size particles. Unless this aerosol is injected into the free troposphere or higher altitudes, e.g., by dust storms or volcanic eruptions, it is typically deposited back to the surface after only a few hundred kilometers of transport due to gravitational settling. On the other hand, fine particle submicron sulfate aerosol has a much longer atmospheric lifetime on the order of a few days in the troposphere and a few years in the stratosphere (see Chapter 5). Gas phase oxidation of reduced sulfur gases and SO_2 represent major indirect sources of fine particle sulfate. As already discussed in Section 8.2.1, submicron sulfate particles are produced from further

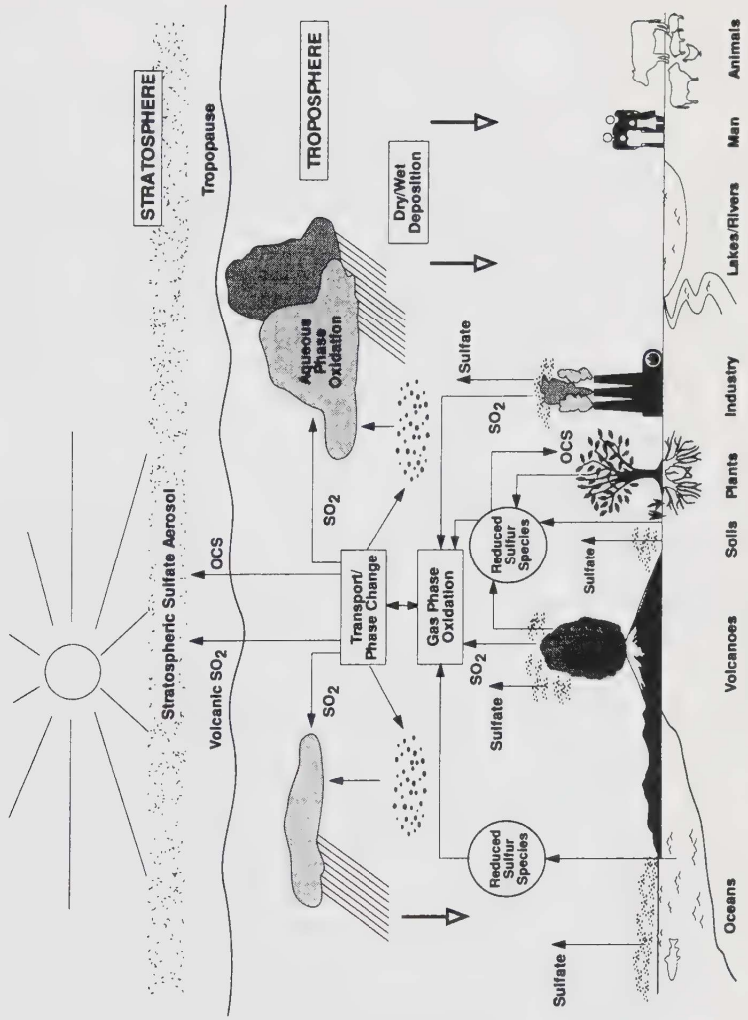


FIGURE 8.1. Major processes involved in the atmospheric sulfur cycle.

oxidation of S(+4) to H_2SO_4 followed by homogeneous or heterogeneous nucleation of sulfuric acid. These particles are believed to be major sources of cloud condensation nuclei (CCNs) in the atmosphere (Twomey, 1971). The cycling of sulfur through the atmosphere is eventually terminated by dry or wet deposition to the Earth's surface, with all its environmental implications as indicated in Figure 8.1.

8.3.1. Emissions

Table 8.4 presents our current best estimates of global sulfur fluxes into the atmosphere. The corresponding values are based on a critical evaluation of recent estimates published by various authors. Estimates of the anthropogenic sulfur flux are well established by now with a relatively narrow range of uncertainty. The results suggest that natural sources represent roughly 30% of the total sulfur emissions into the atmosphere ignoring contributions from sea-salt and soil dust sulfate. Bates et al. (1992b) estimate about 24% globally based on a somewhat lower value for the oceanic sulfur flux. According to the data in Table 8.4, anthropogenic sources contribute about 80% to the emissions in the northern hemisphere (NH) and 30% in the southern hemisphere (SH).

8.3.1.1. Anthropogenic Emissions

The most recent and most detailed estimates to date of anthropogenic sulfur emissions have been presented by Spiro et al. (1992), Hameed and Dignon (1992), and Dignon and Hameed (1989). Figure 8.2 shows a revised update of the historical trend of anthropogenic sulfur emissions since the beginning of the industrial age. Approximately 90–94% of these emissions are from the NH. Based on the data in Figure 8.2, anthropogenic sulfur emissions surpassed natural sulfur emissions in the NH by about 1910 and on a global scale during the decade of the 1950s. This conclusion is further supported by Greenland ice core studies (Mayewski et al., 1990; Neftel et al., 1985) and model calculations (Langner et al., 1992) indicating a dramatic increase in atmospheric sulfate levels in the NH since about 1890. Figure 8.2 also includes the temporal variation in anthropogenic CO_2 emissions over the same period. The similarity between the two trends clearly indicates a strong correlation between man-made sulfur emissions and fossil fuel combustion. Recent estimates suggest that approximately 87–94% of the anthropogenic sulfur in the atmosphere is contributed from fossil fuel combustion, coal coking, and petroleum uses. Based on earlier work by Warneck (1988) and Brimblecombe et al. (1989), we estimate that sulfate and reduced sulfur compounds each represent about 3% of the total anthropogenic sulfur released into the atmosphere. The bulk portion (94%) is emitted as SO_2.

TABLE 8.4 Global Sulfur Emission Estimates (Tg S year^{-1})

Source	H_2S	DMS	CS_2	OCS	SO_2	SO_4	Total[a]
Fossil fuel combustion + industry		Total reduced S: 2.2			70	2.2	71–77 (mid-1980s) (68/6)
Biomass burning	<0.01?	–	<0.01?	0.08	2.8	0.1	2.2–3.0 (1.4/1.1)
Oceans	<0.3	15–25	0.08	0.17	–	40–320	15–25 (8.4/11.6)[b]
Wetlands	0.006–1.1	0.003–0.68	0.0003–0.06	0.0006–0.12	–	–	0.01–2 (0.8/0.2)
Plants + soils	0.17–0.53	0.05–0.16	0.02–0.05	0.01–0.03	–	2–4	0.25–0.78 (0.3/0.2)[c]
Volcanoes	0.5–1.5	–	–	0.01	7–8	2–4	9.3–11.8 (7.6/3.0)
Anthropogenic (total)							73–80
Natural (total, without sea-salt and soil dust)							25–40
Total							98–120

[a]Numbers in parentheses are fluxes from northern hemisphere/southern hemisphere.
[b]Excluding sea-salt contributions.
[c]Excluding soil dust contributions.

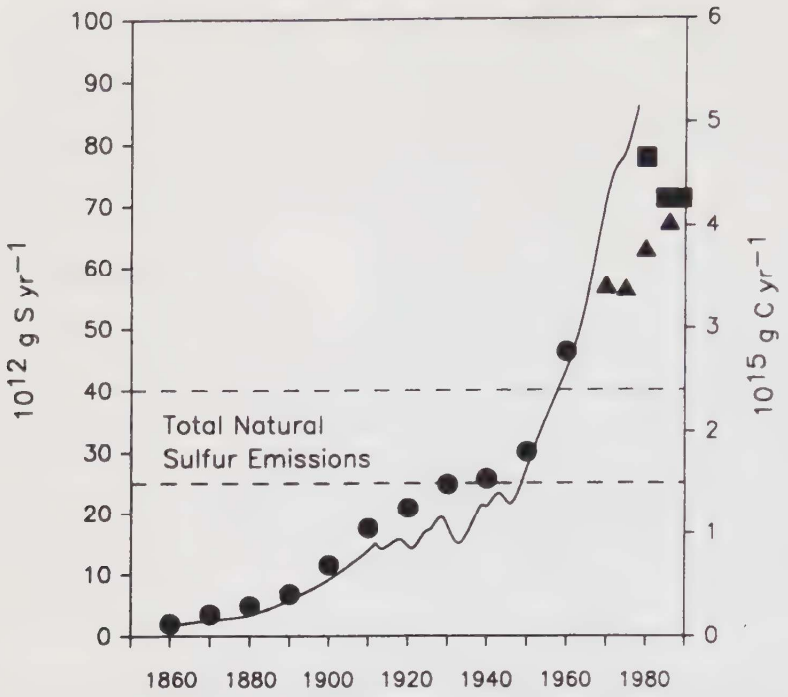


FIGURE 8.2. Global anthropogenic SO_2 and CO_2 emissions since 1860. Data are from Dignon and Hameed (1989; circles), Hameed and Dignon (1992; triangles), and Spiro et al. (1992; squares). Data for CO_2 (solid curve) are from Bolin et al. (1981). The dashed lines indicate the estimated range for the global natural sulfur flux (Table 8.4).

Figure 8.2 shows recent deviations between sulfur and CO_2 emission trends since about the mid-1960s illustrating the effect of abatement policies on SO_x (SO_2 + SO_4^{2-}) emissions in North America and Western Europe. Spiro et al. (1992) also took into account the improved use of sulfur recovery technologies in the former USSR and estimate that global man-made sulfur emissions have actually decreased during the 1980s. On the other hand, the study by Hameed and Dignon (1992) shows a significant geographical shift in anthropogenic sulfur emissions. Asia (not including the former USSR) has become the leading sulfur polluting continent since about 1981 with a continuing increase in anthropogenic sulfur emissions (>20 Tg S $year^{-1}$ in 1986), while those from North America (<15 Tg S $year^{-1}$ in 1986) have steadily declined since about 1970. The emissions from Asia have nearly doubled between 1975 and 1986 mainly because of the increased use of coal combustion in China. On a country-by-country basis, the largest emitters of SO_x in 1986 were the USSR, USA, China, India, and Poland as shown in Figure 8.3.

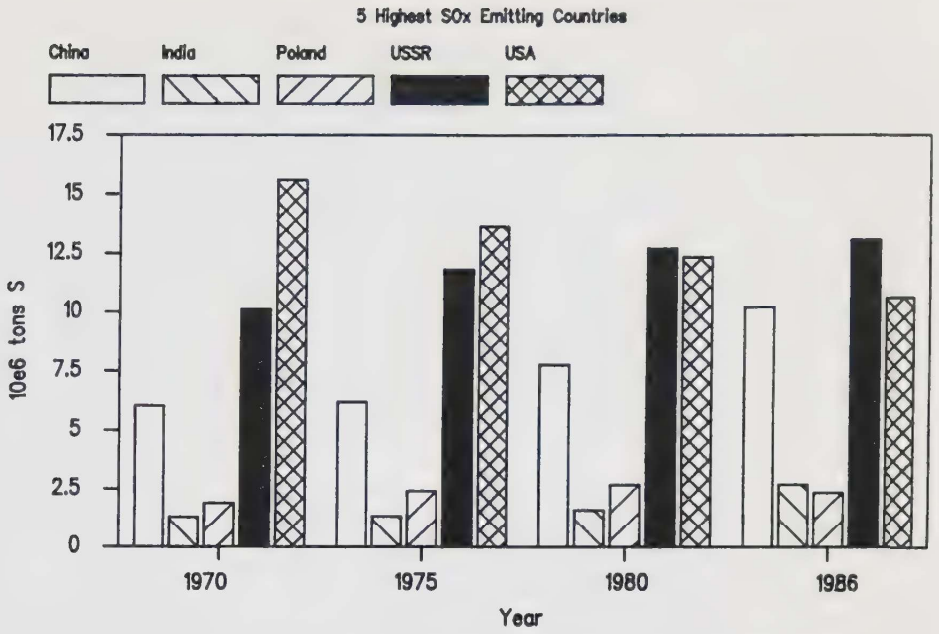


FIGURE 8.3. Recent trends in anthropogenic SO_x emissions from the five highest emitter countries. (Reproduced from Hameed and Dignon 1992, with permission.)

8.3.1.2. Biomass Burning

Approximately 95% of global biomass burning is human-initiated (Bates et al., 1992b). A detailed review of sulfur emissions from biomass burning has been given by Andreae (1991). SO_2 and OCS appear to be the only sulfur compounds emitted in significant amounts, while H_2S and CS_2 emissions are probably on the order of a few per cent of the OCS flux (Chin and Davis, 1993). These minor sulfur compounds (including OCS) are predominantly released from smoldering ash after the end of the active burning phase. Recently Penner et al. (1992) calculated the amount of smoke emitted from biomass burning to be 114 Tg year^{-1}. Using this value and a sulfur/carbon emission ratio of 0.85 g S/kg C (Andreae, 1991), we estimate that about 0.1 Tg S year^{-1} of sulfate is emitted from biomass burning. The uncertainties in all these estimates are high. Even the total burning area is only known with a certainty of about ±50% (Robinson, 1989). However, it appears likely that biomass burning is the dominant atmospheric sulfur source in tropical latitudes (25° N–25° S) during the burning season (Bates et al., 1992b), although on a global annual basis it represents a relatively small source (Table 8.4).

8.3.1.3. Natural Emissions

Measurements of sulfur fluxes from different natural sources have been reviewed by a number of authors, most recently by Andreae and Jaeschke (1992), Bates et al. (1992b), and Aneja (1990). Natural sulfur emissions typically show large spatial and temporal variations which make it difficult to extrapolate individual measurements on a global scale. On the other hand, a significant number of field studies have been conducted over the last two decades resulting in continuous improvements in global flux estimates. Although some of the estimated ranges shown in Table 8.4 are still large, it appears that sulfur emissions from wetlands, plants, and soils may only be of local or regional importance. The most significant natural sulfur sources on a global scale are oceanic and volcanic sulfur emissions. However, our present estimate for the total natural sulfur flux still has an uncertainty of at least ±30% compared with less than ±10% for anthropogenic emissions. Clearly more studies are needed to further reduce these uncertainties.

Oceans

Current estimates of oceanic DMS emissions range from 11.9–15.4 Tg S $year^{-1}$ (Spiro et al., 1992; Bates et al., 1992b; Erickson et al., 1990) to 19–51 Tg S $year^{-1}$ (Andreae and Jaeschke, 1992). Some of the uncertainties in these estimates are due to the calculation of the oceanic DMS flux, which is usually based on measured DMS concentrations in surface seawater and a parameterization scheme for gas exchange across the air–sea interface (e.g., Liss and Merlivat, 1986). Other major uncertainties arise from the temporal and spatial variability of DMS in seawater. The average estimate by Andreae and Jaeschke (1992; 35 Tg S $year^{-1}$) is probably too high due to (a) an overemphasis of data from tropical and upwelling regions, (b) the assumption of a single global value for the vertical transfer velocity v_p, of DMS in the sea-water column, and (c) the lack of wintertime measurements in their data set. Bates et al. (1992b) include winter data and a spatial and seasonal variability of v_p in their estimate. Spiro et al. (1992) and Erickson et al. (1990) use field data reported by Bates and co-workers and calculate a global v_p field based on climatological data.

However, Bates et al. (1992b) likely underestimated DMS emissions from the Southern Ocean by at least a factor of 2. Berresheim (1987) calculated the DMS flux from the ocean area south of 40° S to be 6.4 Tg S $year^{-1}$ based on seasonal primary productivity rates and his measurements during the austral fall season in this region. Bates et al. (1992b) estimate a DMS flux of only 3.5 Tg S $year^{-1}$ from the ocean area between 35° S–80° S. Recent measurements by McTaggart and Burton (1992) and Gibson et al. (1990) show very high DMS concentrations in Antarctic surface waters during the austral summer season, on the average 18.5 nM in open ocean waters and as much as 290 nM in coastal waters. In comparison, the global average DMS sea surface concentration is on the order of

2 nM. Based on their measurements, Gibson et al. (1990) estimate the annual DMS flux from the Antarctic shelf area alone to be 1.3 Tg S $year^{-1}$. This suggests that the global estimate by Bates et al. (1992b) probably represents a lower limit. In summary, we consider the DMS flux range given in Table 8.4 to be the most reasonable estimate at the present time.

The estimated H_2S flux in Table 8.4 is based on recent measurements by Andreae et al. over the North Atlantic and by Yvon et al. over the equatorial Pacific (Table 8.3, references 33 and 34). OCS and CS_2 flux estimates have been adopted from Chin and Davis (1993). The flux of sea-salt sulfate into the atmosphere represents probably the largest uncertainty in all the estimates listed in Table 8.4. Corresponding values have been adopted from Andreae and Jaeschke (1992) bracketing those estimated by Bates et al. (1992b; 131–275 Tg S $year^{-1}$).

Wetlands

Biogenic sulfur emissions from wetlands (tidal flats, coastal salt marshes, freshwater marshes, and swamps) can vary by up to six orders of magnitude in time and space (see, e.g., Aneja, 1990; Adams et al., 1980). Overall, the contributions of wetlands to the atmospheric sulfur cycle are now considered to be of regional but not global importance owing to the relatively small area of wetland regions. Bates et al. (1992b) estimate the global wetland area to be 3.4 $\times 10^6$ km^2 in the NH and 0.3 $\times 10^6$ km^2 in the SH. They estimate a corresponding global sulfur flux of only 0.008 Tg S $year^{-1}$ with approximately 84% of the emissions in the NH. Andreae and Jaeschke (1992) estimate a total flux of 1.76 Tg S $year^{-1}$ with relative contributions from H_2S (57%), DMS (34%), OCS (6%), and CS_2 (3%). We have applied this relative distribution to our present estimate in Table 8.4. Based on the reviews by Andreae and Jaeschke (1992) and Aneja (1990), we consider 2 Tg S $year^{-1}$ as an upper limit.

Soils and Plants

A wide range of reduced sulfur compounds are emitted from soils (Banwart and Bremner, 1975), from crops and other lower plants (Fall et al., 1988), and from trees (Rennenberg, 1991). Extensive studies of these sulfur sources have been conducted in temperate and subtropical latitudes. All these studies have shown a strong positive correlation between sulfur emissions and temperature and light conditions. However, early global estimates based on these observations have drastically overestimated sulfur fluxes from tropical land masses as recent measurements in Amazonia and the Congo rain forest have shown (Table 8.3). In addition to temperature and light intensity, terrestrial sulfur fluxes also depend strongly on plant and soil types and on other factors such as water and nutrient availability. Andreae and Jaeschke (1992) estimate the annual sulfur flux from tropical forests to range between 0.23 and

0.76 Tg S $year^{-1}$ assuming a tropical forest area of 14.5×10^{12} m^2 and an area-based average flux of 30–100 ng S m^{-2} min^{-1}.

For the rest of the total land area (88×10^{12} m^2) they calculate a flux of 3.5 Tg S $year^{-1}$, resulting in a global estimate of 3.8–4.3 Tg S $year^{-1}$. However, their estimate for the extratropical regions is probably too high or miscalculated. Andreae and Jaeschke (1992) state that their corresponding estimate is based on average flux data reported in the natural sulfur emission survey established recently by Guenther et al. (1989) for the area of the United States. However, a corresponding value of only 0.19 Tg S $year^{-1}$ results using the national average flux of 4.0 ng S m^{-2} min^{-1} reported by Guenther et al. (1989). This would add up with the tropical flux estimated by Andreae and Jaeschke (1992) to only 0.42–0.95 Tg S $year^{-1}$ emitted from terrestrial biogenic sulfur sources. Using a somewhat higher total area estimate (Bates et al., 1992b; 1.3×10^{14} m^2), values between 0.48 and 1.01 Tg S $year^{-1}$ are obtained. Corresponding results by Bates et al. (1992b; 0.35 Tg S $year^{-1}$) and Spiro et al. (1992; 0.91 Tg S $year^{-1}$) support this correction of the Andreae and Jaeschke (1992) estimate.

The sulfur emission inventory by Guenther et al. (1989) does not account for a possible recycling or uptake of reduced sulfur gases from the atmosphere by plants and/or soils. Several studies (reviewed by Chin and Davis, 1993) have shown that plant uptake may represent a major sink for atmospheric OCS. In their review Chin and Davis (1993) estimate the global uptake flux of OCS by plants to be ≈ 0.23 Tg S $year^{-1}$ assuming that OCS emissions from vegetation are negligible on a global basis. If we correct our estimated range of 0.48–1.01 Tg S $year^{-1}$ by this value, we obtain the final estimate shown in Table 8.4 for the net global sulfur flux from soils and plants. Fluxes for individual sulfur gases have been derived on a percentage basis as proposed by Andreae and Jaeschke (1992) and Aneja (1990): H_2S, 68%; DMS, 21%; CS_2, 7%; OCS (net), 4%. Also, the estimate by Andreae and Jaeschke (1992) for soil dust sulfate emissions has been adopted here. Overall, the total estimate for the terrestrial biogenic sulfur flux (including emissions from wetlands) bears a large uncertainty second only to that for the flux of sea-salt sulfate into the atmosphere.

Volcanoes

The range of global volcanic sulfur emissions given in Table 8.4 is based on previous estimates by Stoiber et al. (1987; 9.3 Tg S $year^{-1}$) and Berresheim and Jaeschke (1983; 11.8 Tg S $year^{-1}$). Estimated fluxes for individual sulfur compounds are largely based on the work of Berresheim and Jaeschke (1983) and for OCS and CS_2, the review by Chin and Davis (1993). Estimates for the hemispheric contributions (72% from the NH, 28% from the SH) have been adopted from Bates et al. (1992b).

Although Table 8.4 shows a relatively narrow range for the global volcanic sulfur flux, the corresponding year-to-year variation in this flux can be very

large. The estimated annual average flux depends very much on the period over which the sulfur flux has been averaged and on the frequency of large explosive eruptions as well as the amount of non-eruptive contributions during the same period. Berresheim and Jaeschke (1983) emphasized that their average flux estimate for the period 1961–1979 was probably somewhat low due to the lack of direct measurements during highly explosive eruptions. However, over the last decade sulfur fluxes from large eruptions have been well documented by airborne and/or remote sensing measurements. The eruptions of El Chichon in 1982 and Pinatubo in 1991 alone contributed about 3 and 7.5 Tg of S to the atmosphere, respectively (A. Krueger, 1992, personal communication). This suggests that annual volcanic sulfur emissions (eruptive plus non-eruptive) are on the order of at least 10% of the total anthropogenic sulfur flux into the atmosphere and may range up to 30% during years with highly explosive eruptions.

8.3.2. Chemical Transformations and Mechanisms

In this section we shall discuss results obtained from laboratory and field studies that have significantly contributed to our understanding of atmospheric sulfur chemistry. Mechanistic models derived from these results will be discussed and modifications will be proposed where deemed appropriate based on our current knowledge. We will mainly focus on the atmospheric transformations of DMS in the remote marine atmosphere, and those of H_2S, CS_2, OCS, and SO_2 in the remote marine and continental atmosphere. By comparison, SO_2 oxidation reactions in the polluted atmosphere will be discussed only briefly. For more details concerning the role of SO_2 as an atmospheric pollutant the reader is referred to Chapters 1, 4, and 12. We would also like to refer the reader to the review by Hansen and Eatough (1991) for a detailed discussion of the atmospheric chemistry of organic S(+6) pollutants (HMSA, $MMSO_4$, $DMSO_4$, and $BHMSO_2$), which have not been considered in the following text. Figure 8.4 gives a schematic overview of some of the more important reduced sulfur compounds in the atmosphere and what are thought to be their principal reaction and removal pathways.

8.3.2.1. The Remote Marine and Continental Atmosphere

In the *remote* marine atmosphere the most important reactive sulfur gas is DMS. Other reduced sulfur compounds such as H_2S and CS_2 are believed to contribute less than 20% to S(+4) and S(+6) levels over the remote oceans. The polluted marine atmosphere would include mainly coastal and open ocean regions where continental air masses predominate. Field measurements have shown that large

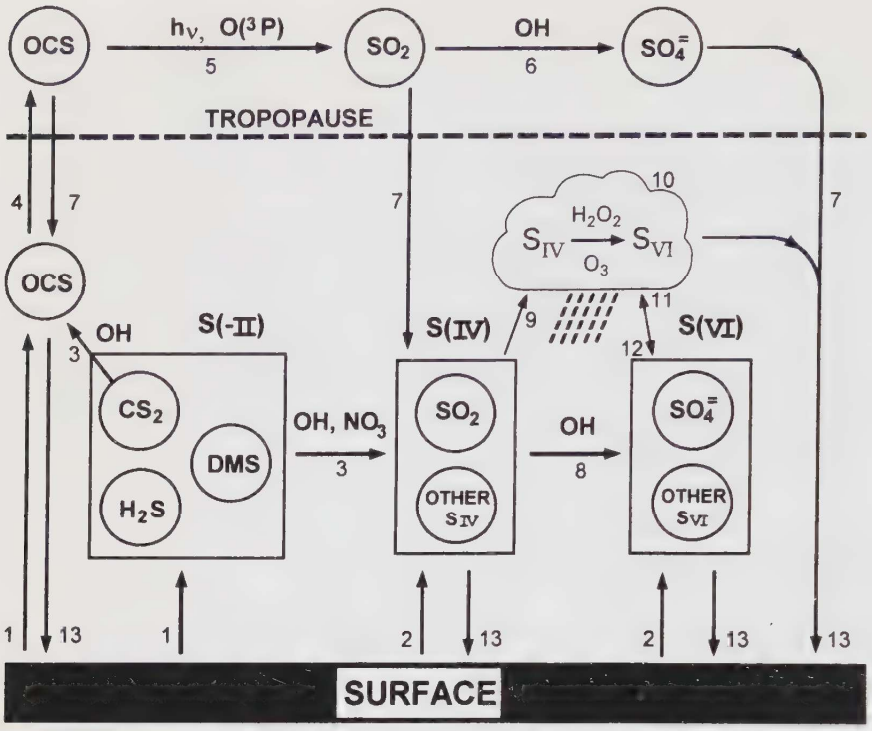


FIGURE 8.4. Major pathways of reduced and oxidized sulfur compounds in the atmosphere: (1) emission of DMS, H_2S, CS_2, and OCS; (2) emission of S(+4) and S(+6); (3) oxidation of DMS, H_2S, and CS_2 by OH, and DMS by NO_3 in the troposphere; (4) transport of OCS into the stratosphere; (5) photolysis of OCS or reaction with $O(^3P)$ to form SO_2 in the stratosphere; (6) oxidation of SO_2 in the stratosphere; (7) transport of stratospheric OCS, SO_2, and sulfate into the troposphere; (8) oxidation of SO_2 and other S(+4) products by OH in the troposphere; (9) absorption of S(+4) – mainly SO_2 – into hydrosols (cloud/fog/rain droplets, moist aerosol particles); (10) liquid phase oxidation of S(+4) by $H_2O_2(aq)$ and $O_3(aq)$ in hydrosols (and by O_2 in the presence of elevated levels of catalytic metal ions); (11) absorption/growth of S(+6) aerosol – mainly sulfate – into hydrosols; (12) evaporation of cloud-water leaving residual S(+6) aerosol; (13) deposition of OCS, S(+4), and S(+6). The SURFACE bar represents anthropogenic and/or natural sources and sinks (e.g., industry, soils, plants, seawater, ice sheets) depending on the type of environment being discussed.

oceanic regions in the northern hemisphere, in particular the North Atlantic, can be periodically influenced by long-range advection of air from bordering industrialized countries (Table 8.3). The major impact of these anthropogenically influenced air masses on marine atmospheric sulfur is to further enhance nss-SO_4^{2-} levels over the oceans via the transport of both anthropogenic SO_2 and sulfate. They also increase the percentage contribution of H_2S and CS_2 to the total reduced sulfur observed in the marine atmosphere.

DMS Oxidation in the Remote Marine Atmosphere

As will be discussed in detail in Section 8.4.1, one of the centrally important issues surrounding oceanic emissions of DMS is its potential role as a climate-modulating species. The general mechanism by which this might occur involves the oxidation of the sulfur atom in DMS to the +6 state followed by heteromolecular nucleation which leads to the formation of new CCN particles. However, both theoretical considerations as well as experimental observations suggest that only the fraction of DMS that is oxidized to gas phase H_2SO_4 plays a significant role in new CCN formation (e.g., Kreidenweis and Seinfeld, 1988). The two most important sulfur reactants involved in this production are the species SO_2 and SO_3. In the case of SO_2, gas phase H_2SO_4 is produced via its reaction with OH radicals; for the species SO_3, it is reaction with gas phase H_2O. Since the yields of both SO_2 and SO_3 from DMS are strongly mechanism-dependent, any quantitative assessment of the DMS–CCN linkage is critically dependent on there being available a detailed understanding of the DMS oxidation scheme.

Historically, both field observations and laboratory studies have contributed to our current understanding of atmospheric DMS chemistry. For example, early field measurements of MSA in atmospheric aerosols (Panter and Penzhorn, 1980) gave the first indication that this compound and possibly other organic sulfur compounds were produced in the atmospheric oxidation of DMS. Similarly, since the early work of Cox and Sandalls (1974), a number of photochemical chamber studies involving DMS–NO_x-air mixtures have identified still other DMS oxidation products and have also led to the investigation of the relative yields of these products as function of varying experimental conditions. In general, all studies seem to agree that SO_2 and MSA(g) are two of the major products from the DMS + OH reaction. However, the results from individual research groups have strongly disagreed with respect to the relative yields of these products. The chamber studies by Niki et al. (1983) and Hatakeyama et al. (1985) suggest that MSA is the dominant product, with lesser amounts of SO_2 being formed. By contrast, the studies by Yin et al. (1986) and Grosjean (1984), although qualitatively showing similar products, indicate quite different relative yields of SO_2 and MSA, SO_2 being by far the dominant product. Similar results were also obtained in a more recent study by Yin et al. (1990) involving an outdoor photochemical chamber.

At this time there appears to be no simple explanation for the major differences between the results of Hatakeyama et al. and Yin and co-workers. Differences in chamber temperatures and concentration levels of initial reactants have been most frequently cited as the reason(s) for the observed differences; but no experimental study has yet confirmed this. In spite of these apparent difficulties, chamber studies have provided a basis for examining the larger mechanistic picture for the oxidation of DMS. In this context they have been instrumental in

conceptually identifying potentially important reactive intermediates as well as more stable products such as DMSO and $DMSO_2$. Both of the latter species have now been observed in recent field studies (see Section 8.2.2).

With respect to providing "definitive" answers to DMS oxidation product yields in the remote MBL, however, chamber studies as previously configured appear to have severe limitations. The reasons are twofold. (1) The surface-to-volume ratio of a typical irradiation chamber is orders of magnitude greater than that of a real MBL atmosphere, thus leading to abnormally high surface loss rates for some products and heterogeneous surface production of others. (2) The mixing ratios of the DMS–NO_x reactants in most chamber studies exceed those in the remote MBL by several orders of magnitude. For example, NO levels in the remote MBL are typically 2–8 ppt (Davis et al., 1987; McFarland et al., 1979) (the latter NO mixing ratio corresponds to approximately 8–25 ppt of NO_x) and DMS levels are 10–300 ppt (see Section 2.2). By comparison, DMS mixing ratios in chamber studies have ranged from 0.3 to 20 ppm and those of NO_x from 0.2 to 18 ppm. The latter levels of reactants can dramatically alter the competitive kinetics of many of the more critical DMS oxidation steps. Thus they can potentially lead to significantly different final product yields as compared with those found under remote marine atmospheric conditions.

Detailed kinetic studies designed to assess the aforementioned complications in the DMS oxidation scheme have been the focus of several laboratory investigations in recent years. These have been critically reviewed by other authors (e.g., Turnipseed and Ravishankara, 1993; Tyndall and Ravishankara, 1991; Yin et al., 1990) and thus only a brief summary will be presented in this section of the text for purposes of aiding the reader in the follow-on discussions of DMS field studies. Later in the text a more comprehensive discussion of the findings from these earlier kinetic studies will be presented. For reader convenience a summary of recommended rate constants for reactions currently thought to be important in the atmospheric oxidation of DMS is also provided in Table 8.5(a).

Current evidence suggests that the atmospheric oxidation of DMS is initiated by one of two species, OH or NO_3. The OH species dominates during daylight hours and NO_3 at night. However, the relative importance of these two pathways is most likely a strong function of latitude, altitude, and season of the year, reflecting significant variations in the levels of both NO_x and HO_x (see discussion later in text). The rate constant for the DMS + OH reaction alone (Table 8.5(a)) suggests a DMS lifetime of approximately 1 day assuming a daily average OH concentration of 2.5×10^6 molecules cm^{-3}.

A number of details concerning the DMS + OH and DMS + NO_3 oxidation mechanisms have been revealed to date. For example, laboratory studies by Hynes et al. (1986) have shown that the DMS + OH reaction branches into two channels: (1) hydrogen abstraction from a methyl group, forming the radical product

TABLE 8.5(a) Rate Constants for Some Important Reactions in the Atmospheric Oxidation of DMS

Reaction	A[a]	E/R[b]	k(298 K)[a]	Reference(s)
$OH + (CH_3)_2 \rightarrow CH_3SCH_2 + H_2O$	960	234	440	1
$OH + (CH_3)_2S + M \leftrightarrow (CH_3)_2SOH + M$ $(CH_3)_2SOH + O_2 \rightarrow$ products	[c]	[c]	170	1, 2
$NO_3 + (CH_3)_2S \rightarrow CH_3SCH_2 + HNO_3$	19	−520	110	2
$Cl + (CH_3)_2S \rightarrow CH_3SCH_2 + HCl$	18000	0	18000	3
$Cl + (CH_3)_2S + M \rightarrow (CH_3)_2SCl + M$	6600	−260	16000	3
$IO + (CH_3)_2SO \rightarrow (CH_3)_2SO + I$			< 1.2	2
$OH + (CH_3)_2SO \rightarrow$ products			8100	4, 5
$NO_3 + (CH_3)_2SO \rightarrow NO_2 + (CH_3)_2SO_2$			17	5
$Cl + (CH_3)_2SO \rightarrow$ products			7400	5
$CH_3SCH_2 + O_2 + M \rightarrow CH_3SCH_2O_2 + M$			570[d]	6
$CH_3SCH_2O_2 + NO \rightarrow CH_3SCH_2O + NO_2$	1010	−130	1550	6, 7
$CH_3SCH_2O + M \rightarrow CH_3S + CH_2O + M$			[e]	7, 8
$CH_3SCH_2O_2 + HO_2 \rightarrow CH_3SCH_2OOH + O_2$	60	−700	630	2[f]
$CH_3S + O_2 + M \rightarrow CH_3SOO + M$	0.14	−1550	25	9[g]
$CH_3SOO + M \rightarrow CH_3S + O_2 + M$	17400[h]	3430	0.174[h]	9[g]
$CH_3S + O_2 \rightarrow$ products			< 0.0006	9, 10
$CH_3S + O_3 \rightarrow$ products	200	−290	530	11
$CH_3S + NO_2 \rightarrow CH_3SO + NO$	2060	−320	6030	11
$CH_3SOO + O_3 \rightarrow$ products				11[i]
$CH_3SOO + NO_2 \rightarrow$ products	(2200)[j]	(0)[j]	(2200)[j]	11
$CH_3SOO + NO \rightarrow$ products	(1100)[k]	(0)[k]	(1100)[k]	11
$CH_3SO + O_3 \rightarrow$ products			100	10
$CH_3SO + NO_2 \rightarrow$ products			1200	12

[a]Units are 10^{-14} cm^3 molecule^{-1} s^{-1} except where otherwise indicated.

[b]Units are degrees Kelvin.

[c]The effective rate constant for *irreversible* addition at 298 K is $k = (4.1 \times 10^{-31}[O_2])/(1 + 4.1 \times 10^{-20}[O_2])$.

[d]P = 760 Torr.

[e]Generally assumed to be very fast; recent experimental work (refs 6 and 7) is consistent with this assumption.

[f]Arrhenius parameters estimated based on known parameters for HO_2 reactions with CH_3O_2, $C_2H_5O_2$, and $CH_3C(O)O_2$. Products are estimated based on results from the $CH_3O_2 + HO_2$ reaction.

[g]Rate constants are for 760 Torr air; they are estimated to be 10 times faster than those measured (ref. 8) in 80 Torr He.

[h]Units are 10^7 s^{-1}.

[i]$k < 8 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} at T = 227 K.

[j]Based on data obtained over temperature range 227–246 K.

[k]Based on data obtained over the temperature range 227–256 K.

1 Hynes et al. (1986), *J. Phys. Chem.*, **90**, 4148; 2 Atkinson et al. (1992), *J. Phys. Chem. Ref. Data*, **21**, 1125; 3 Stickel et al. (1992), *J. Phys. Chem.*, **96**, 9875; 4 Hynes et al. (1992), *12th Int. Symp. on Gas Kinetics, Reading*, Abstract G6; 5 Barnes et al. (1989), in *Biogenic Sulfur in the Environment*, Saltzman and Cooper, Eds, *ACS Symp. Ser.*, Vol. 393, pp. 476–488; 6 Wallington et al. (1993), *J. Phys. Chem.*, **97**, 8442; 7 Zhao, Stickel, and Wine (1994), personal communication; 8 A. Ravishankara (1993), personal communication; 9 Turnipseed et al. (1992), *J. Phys. Chem.*, **96**, 7502; 10 Tyndall and Ravishankara (1989), *J. Phys. Chem.*, **93**, 4707; 11 Turnipseed et al. (1993), *J. Phys. Chem.*, **97**, 5926; 12 Domine et al. (1990), *J. Phys. Chem.*, **94**, 5839.

CH_3SCH_2, and (2) addition of OH to the sulfur atom. The abstraction channel dominates in the absence of O_2, whereas, the addition channel involves oxidation of the adduct with O_2 in competition with adduct decomposition back into DMS + OH. In the presence of O_2 both channels have equivalent rates at approximately 285 K, with H abstraction dominating at higher temperatures. Both the addition and abstraction branches as well as the overall observed rate constant, k_{obs}, are shown as a function of temperature in Figure 8.5. Concerning the second DMS initiator species, NO_3, recent laboratory studies suggest that the most likely primary products of this reaction are HNO_3 and CH_3SCH_2. As a result, both the DMS/OH abstraction channel and the DMS/NO_3 reaction lead to the same sulfur-containing free radical, CH_3SCH_2 (e.g., see Figure 8.6(a)). Thus the ensuing chemistry from these two different initiator species is indistinguishable.

Field studies aimed at understanding the oxidation mechanism of atmospheric DMS have typically focused on one of two aspects of this chemistry: (a) the influence of temperature on the relative distributions of measurable stable products; (b) assessments of the diurnal trends in DMS and its associated products in the marine boundary layer. As illustrated in several proposed DMS oxidation schemes (Turnipseed and Ravishankara, 1993; Bandy et al., 1992; Yin et al., 1990; see also Figures 8.6(a) and 8.6(b)), the chemical degradation of DMS involves numerous competitive kinetic steps. Among the more important of these is the aforementioned OH initiation step which can involve either addition or abstraction. Both processes are temperature-dependent, but so also are many

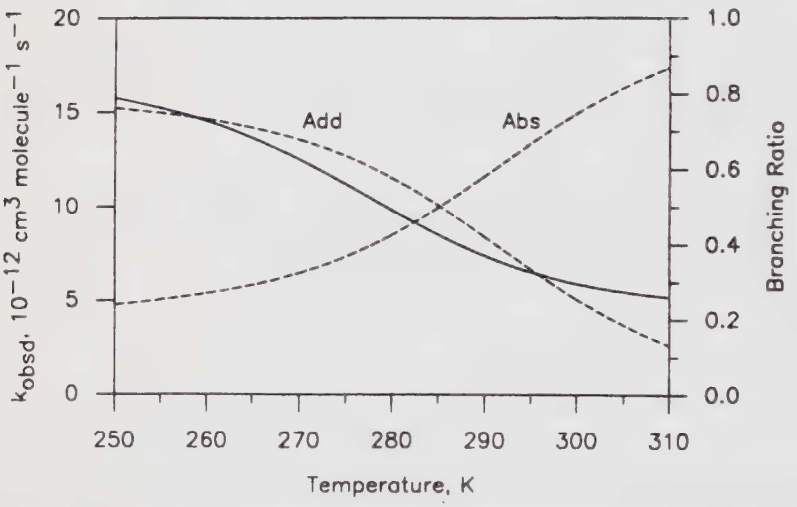


FIGURE 8.5. Temperature dependence of the branching ratio between the addition (Add) and abstraction (Abs) channels in the DMS + OH reaction (dashed curves). Also shown is the overall observed rate constant k_{obsd} (solid curve).

other critical DMS reactions, and still others have a critical dependence on the absolute levels of photogenerated free radicals. As a result, the DMS product distribution for a given set of environmental conditions as well as the diurnal trends in DMS might be expected to have a significant but perhaps complex dependence on both temperature and the level of photochemical activity.

Qualitatively, some field studies seem to confirm aspects of the above cited predictions, while in other cases there seem to be conflicting results. For example, as discussed earlier in the text, two of the known end-products of the OH-initiated degradation of DMS are H_2SO_4 (sulfate; see Figure 8.4) and MSA. Of the two, sulfate formation is now viewed mechanistically as defining the higher-energy pathway. In fact, field studies over remote tropical and subtropical ocean areas have shown that the mole ratio of MSA(p)/nss-SO_4^{2-} in aerosol ranges from about 0.02 to 0.1. By contrast, at higher latitudes this ratio has been found to vary from 0.15 to 1 (Huebert et al., 1993; Bates et al., 1992a; Ayers et al., 1991; Savoie and Prospero, 1989; Berresheim, 1987; Saltzman et al., 1983). Collectively, therefore, these data do suggest an inverse correlation of the MSA(p)/nss-SO_4^{2-} ratio with temperature. Conflicting with this simple interpretation, though, are seasonal data obtained at Cape Grim, Tasmania (40° S) and Norfolk Island (30° S) in the South Pacific Ocean, both of which show an average maximum MSA(p)/nss-SO_4^{2-} ratio of 0.1–0.2 during the austral summer and a minimum of 0.02–0.06 during winter (Ayers et al., 1991; Saltzman et al., 1986). Whether this is indeed a conflict or simply a reflection of uncertainties in the data is not clear at this time, (see discussion on methodology employed in evaluating the quantity nss-SO_4^{2-}, Section 8.2.2). Such data also raise some important questions concerning our level of understanding of the sources of non-sea-salt sulfate. For example, the assumption that DMS oxidation accounts for the bulk of the observed nss-SO_4^{2-} may be poorly founded in some cases. Several airborne field studies conducted over low- and mid-latitude oceanic regions have produced data showing an increase in the SO_2 mixing ratio with increasing altitude above the MBL. These observations suggest that the source of MBL non-sea-salt sulfate could have resulted from entrainment of SO_2 air from the FT rather than oxidation of DMS (e.g., Table 8.3, references 12, 60, and 74; Bandy et al., 1992). Possible sources of high-altitude sulfate include long-range transport of anthropogenic SO_2 and/or SO_4^{2-}, volcanic emissions, and convective pumping of precursor species (e.g., DMS, H_2S, CS_2) into the FT (Chatfield and Crutzen, 1984). As discussed earlier in the text, a third factor that may have influenced the reported trend in the MSA/nss-SO_4^{2-} ratio data is this ratio's dependence on the levels of photochemical free radicals, the latter being a strong function of latitude and/or season of the year. This point will be discussed in greater detail later in the text.

The second type of field study for which considerable data have been generated has involved the investigation of DMS diurnal trends under MBL

conditions. Under stable meteorological conditions, simple photochemical models predict that for a species such as DMS, having an ocean source and an OH controlled lifetime of approximately 1 day , maximum levels in the DMS mixing ratio should be observed in the early morning hours and minimum levels during the late afternoon. Assuming a fairly constant DMS flux from the ocean surface and no major loss of DMS at night due to NO_3, both the maximum and minimum DMS levels (i.e., points of inflection) should correspond to those times when the DMS flux is exactly balanced by the rate of photochemical removal of DMS. In fact, the results from several field studies designed to look for this diurnal variation have been moderately encouraging, typically showing diurnal amplitude ratios of 1.4–2.3 (Table 8.3) (e.g., Saltzman et al., 1995; Saltzman and Cooper, 1989; Thompson et al., 1993). However, disagreements between observations and predictions have also surfaced, indicating that the uncertainties in these comparison studies are still quite substantial. The uncertainties include (a) the use of sea-to-air fluxes of DMS calculated from oceanic DMS concentration measurements and thin film mass transport approximations (see Section 8.3.1.3), (b) the absence of MBL height data over the time period of DMS measurements, (c) the absence of detailed information on the dynamic exchange of air masses between the MBL and FT, (d) the lack of a detailed description of the daytime photochemical environment, and (e) the lack of a detailed description of the night-time chemical environment as driven by NO_3 chemistry.

In still other diurnal studies the focus of investigation has been on correlations between DMS and DMS oxidation products. For example, during recent shipboard measurements off the Washington coast, Bandy et al. (1992) observed that in daylight periods when DMS was highest (e.g., 180 ppt), SO_2 levels remained statistically nearly the same (e.g., 25 ppt) as on days when DMS levels were low. Bandy et al. estimate that for the season and meteorological conditions encountered and with all OH-oxidized DMS being converted to SO_2, the level of SO_2 observed should have exceeded 60 ppt. These authors further argue that the low SO_2 values cannot be explained by the action of a strong non-photochemical sink, since this would have necessarily resulted in the total depletion of SO_2 at night. Average daytime and night-time SO_2 levels were 30 and 24 ppt, respectively. Bandy et al. suggest that their data appear to be more consistent with the idea that one of the major sources of SO_2 was entrainment from the FT and that SO_2 was basically kept in steady state due to surface deposition. Thus these authors hypothesize that the oxidation of DMS does not include the major formation of SO_2 but rather the production of the sulfate forming species SO_3.

During another shipboard study in the equatorial Pacific, Yvon et al. (reference 75, Table 8.3) recorded fast time resolution measurements of SO_2 which, like the data of Bandy et al., also showed no diurnal variation. By contrast, both DMS and H_2S measurements recorded at the same time revealed very significant

variations in their mixing ratios as a function of time of day. From still other measurements reported in the equatorial Pacific by Huebert et al. (1993), very high average DMS/SO_2 mole ratios were recorded (i.e., 18) and again no correlation was observed between DMS and SO_2. Assuming no SO_2 measurement difficulties, the results from the latter two studies, like those reported by Bandy et al., suggest that at each of these sampling sites SO_2 was a minor DMS oxidation product and that the levels of this species were controlled by other sources.

As of this date the only strong correlation reported between DMS and SO_2 in the remote MBL is the seasonal correlation observed at Amsterdam Island (37°50′ S, 77°30′ E) in the Indian Ocean (Putaud et al., 1992). However, as pointed out by Huebert et al. (1993), it is quite possible that even with SO_2 being formed only as a minor product of DMS oxidation, a long-term seasonal coherence between SO_2 and DMS might be found provided that "on average" atmospheric SO_2 levels were controlled by DMS oxidation and not by external sources.

In a still more comprehensive field study by Berresheim et al. (1993a), simultaneous measurements of the gas phase species DMS, DMSO, $H_2SO_4(g)$, MSA(g), and CCN particles were made at a Pacific coastal site in the state of Washington. This study was conducted in parallel with the offshore measurements reported by Bandy et al. (1992). The results from this study indicate that all the measured sulfur gases showed significant diurnal variations, and in most cases these trends were all in phase with each other. Berresheim et al. (1993a) interpreted the observed low mixing ratios for MSA(g) and $H_2SO_4(g)$ relative to DMSO as an indication that DMSO formation was the most important reaction pathway in the oxidation of DMS. Statistical evidence was also obtained which indicated a significant correlation between individual sulfur species and CCN levels.

The photochemical interpretation of the Pacific coast data was not provided in the Berresheim et al. (1993a) publication but has been examined in the text that follows. In this analysis we have used the fact that all gas phase species were measured nearly simultaneously in time. Thus, based on the assumption that the system was in photochemical equilibrium, the DMS and DMSO field data have been used here to assess the relative importance of the addition versus abstraction channels in the oxidation of DMS. We have explored this possibility here by selecting data from the sampling time period of April 24 and 25. During this time period meteorological conditions were reported to be sunny with air advected from the Pacific Ocean, providing optimal conditions for a photochemical study. Taking in this case only those data recorded during the solar window (from 9.30 to 15.00 h, local time), median values for the mixing ratios of DMS, DMSO, $H_2SO_4(g)$, and MSA(g) were reported to be 19.4, 0.95, 0.06, and 0.015 ppt, respectively. For the specific case of DMSO, the atmospheric lifetime is

controlled by its reaction with OH and was estimated to be approximately 1 h. The latter estimate was based on an average midday OH level of 3×10^6 molecules cm^{-3} and a value of $k_{OH,DMSO} = 1 \times 10^{-10}\,cm^3\,molecule^{-1}\,s^{-1}$ (Table 8.5(a)). Under these conditions application of the photostationary state approximation allows the rate of formation of DMSO to be equated to its rate of destruction, i.e.

$$k_{OH,DMS}[OH][DMS] \times BR = k_{OH,DMSO}[OH][DMSO] \tag{8.3}$$

where BR is the branching ratio for the OH addition channel (see Figures 8.5, and 8.6(a)). Given the cited daytime mixing ratios of DMS and DMSO and an average air temperature of 280 K, we calculate a value for the parameter BR of 0.5. For the same temperature the kinetic data shown in Figure 8.5 give a value for the addition channel branching ratio of 0.57. As shown in Figure 8.6(a), the latter channel is the only one leading to the formation of the product DMSO.

The largest uncertainty in the evaluation of the branching ratio is clearly the uncertainty associated with the estimate of the midday average OH concentration. Given that this could be as large as a factor of two, the level of agreement between the field observations and the DMS/OH kinetic data (Figure 8.5) could be viewed as either fortuitous or as reassuring. Taking the more optimistic attitude, if the lifetime of both H_2SO_4(g) and MSA(g) with respect to deposition on pre-existing particles is taken to be 1 h (Berresheim et al., 1993a), and if it is further assumed that all chemical intermediates leading to the formation of MSA(g) and H_2SO_4(g) are at photochemical equilibrium, an estimate can also be made of the rates of production of the latter products relative to the formation of the addition channel product DMSO. For this case, based on the cited ratio of DMSO to MSA, we estimate that the rate of production of MSA from DMS was several factors of 10 lower than that of the addition channel product DMSO. For H_2SO_4(g) the evaluation is not as straightforward in that this species could have been formed either via DMS-generated SO_3 or from gas phase OH-oxidized SO_2. The SO_2 in turn may have been formed from the oxidation of DMS and/or derived from an anthropogenic source. Making the most favorable assumption, i.e., that all H_2SO_4(g) was formed from SO_3 whose origin was DMS oxidation, the observed ratio of H_2SO_4(g) to DMSO would suggest that the SO_3 yield from DMS was very minor relative to that of DMSO. Concerning the yield of SO_2 from DMS, the Pacific coast data are even more difficult to interpret than for SO_3 owing to the strong possibility of rapid heterogeneous processes (Chameides and Stelson, 1992; Hegg, 1985). Thus no definitive statement can be made about the yield of this species from DMS other than it had to be smaller than that for the OH/DMS addition channel, i.e., < 0.5.

In general, the above-cited Pacific coast results do not support Bandy et al.'s (1992) suggestion that for their study SO_3 was the most likely major

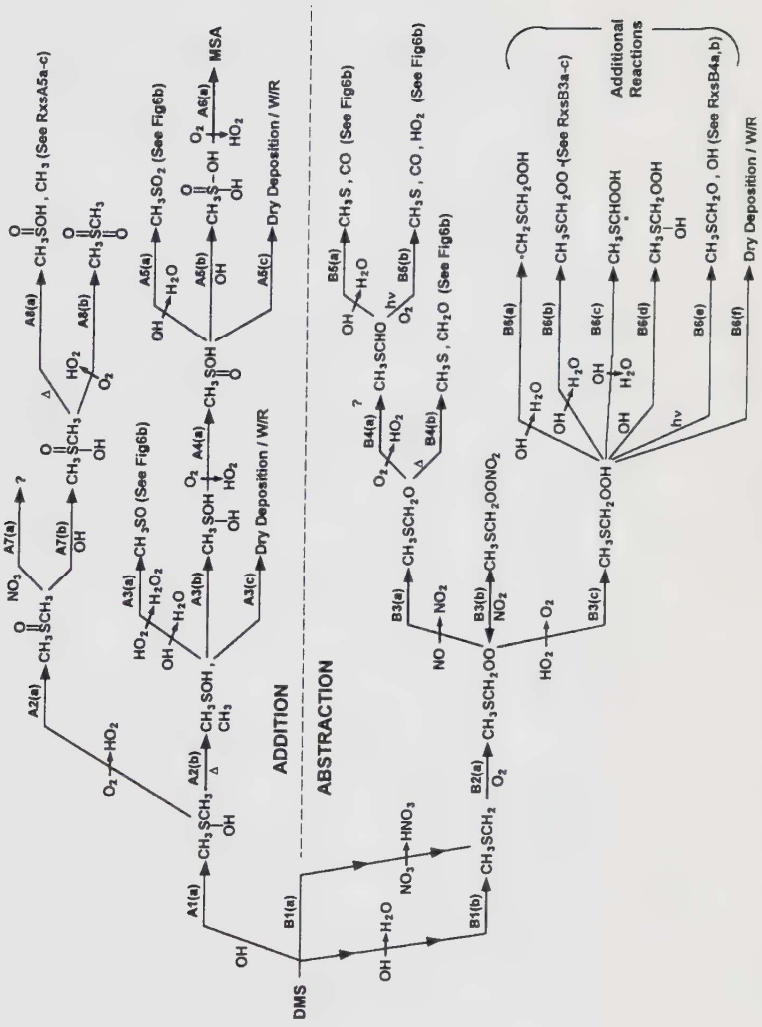


FIGURE 8.6(a). Proposed mechanism for the oxidation of DMS in the remote marine atmosphere: abstraction and addition channels in the OH- and NO_3-initiated oxidation of DMS. W/R = wash-out/rain-out.

"intermediate" product formed in the degradation of DMS. But they do tend to support Bandy et al.'s conclusion that SO_2 was not a major product from DMS oxidation. In both cases, however, it is possible that differences in conditions on the ship versus the coastal study may have influenced the final results.

The Pacific coast results also appear to be in general agreement with recent speculations by Huebert et al. (1993) concerning DMS, SO_2, MSA, and nss-SO_4^{2-} data recorded in the equatorial Pacific. The latter authors, based on the relative lifetimes for the aforementioned species, have speculated that their results were only consistent with the idea that the major products from DMS oxidation were DMSO and/or $DMSO_2$. As noted above, this result would seem to be in agreement with those reported by Berresheim et al. (1993a). On closer

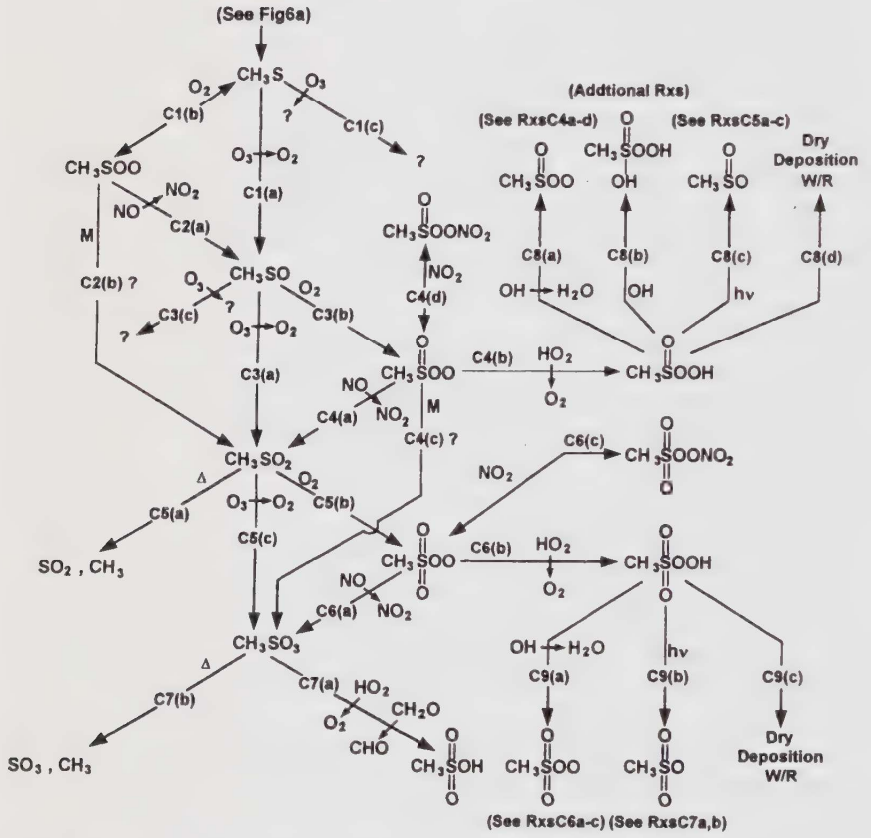


FIGURE 8.6(b). Proposed mechanism for the oxidation of DMS in the remote marine atmosphere: mechanistic scheme for reactions involving CH_3SO_x species. WR = wash-out/rain-out.

inspection, however, one finds that the average MBL temperature reported for this study was quite high, i.e., 300 K (Thompson et al. (1993)). For this case, taking the temperature dependence of the addition versus abstraction pathway in the DMS + OH reaction mechanism as indicated in Figure 8.5, one would predict a corresponding DMSO addition channel rate that was no more than 25% of the total destruction rate of DMS. Thus their data may require a somewhat different explanation as proposed later in this text.

As stated previously, laboratory kinetic studies have been as important as field studies in the elucidation of the atmospheric fate of DMS. In the text that follows, we will discuss in further detail the previous reviews by Turnipseed and Ravishankara (1993), Tyndall and Ravishankara (1991), and Yin et al. (1990). In addition, the present authors will add their own insights to the discussion based on their assessment of more recent field, laboratory kinetic, and modelling studies. Some of the kinetic results with respect to the OH-initiated DMS oxidation have already been mentioned. For example, while it is now certain that hydrogen abstraction from DMS forms the new radical CH_3SCH_2, there is somewhat less certainty about the nature of the product resulting from the OH addition channel. In general, though, the observed O_2 dependence of this reaction suggests that the addition channel yields DMSO as the major product rather than methanesulfenic acid, CH_3SOH (Stickel et al., 1993b). The recent field data reported by Berresheim et al. (1993a), showing a significant correlation between DMS and DMSO mixing ratios in MBL air, also add considerable weight to the argument that DMSO is the major product from the OH addition channel. As shown in Figure 8.6(a), the subsequent reaction of DMSO is somewhat more speculative. Recent kinetic investigations (Hynes et al., reference 4, Table 8.5(a)) as well as sulfur field studies in the Antarctic in which both DMSO and $DMSO_2$ were measured (Eisle and Berresheim, unpublished results) suggest that methanesulfinic acid, $CH_3S(O)OH$, rather than $DMSO_2$ is the more likely dominant stable end-product from the DMS + OH addition channel.

A common mechanistic scheme employed to describe the further oxidation of the CH_3SCH_2 radical involves the sequence of reactions shown in Figure 8.6(a) labelled B2(a), B3(a), and B4(b). This reaction sequence includes the addition of O_2 to form a peroxy radical followed by reaction with NO and the subsequent thermal decomposition of the radical species CH_3SCH_2O to form the CH_3S radical and formaldehyde. As shown in Figure 8.6(b), the chemistry of the CH_3S radical is speculated to be the principal source of the products SO_2, SO_3, MSA(g), and H_2SO_4. As a consequence, the ensuing chemistry from this species has received the greatest attention by laboratory kineticists. However, as shown in Figure 8.6(a), the relative importance of CH_3S chemistry versus other possible DMS oxidation pathways will depend very strongly on the exact conditions encountered in the remote marine atmosphere.

For conditions defined by the tropical and subtropical remote MBL, where NO levels are typically 2–8 ppt (Davis et al., 1987), it appears that the dominant reaction of the peroxy radical, CH_3SCH_2OO, is not with NO but rather with HO_2 radicals. The resulting product should be a stable peroxide species, CH_3SCH_2OOH. For example, assuming an average MBL mixing ratio for NO of 4 ppt and an average daytime value for HO_2 of 4×10^8 molecules cm^{-3} (Davis et al., 1993), the rate for the HO_2 reaction channel is nearly twice that of the NO reaction. Thus, in analogy with the well-studied CH_3OOH species, one might speculate that CH_3SCH_2OOH would undergo a manifold of reactions, i.e., B6(a), B6(b), B6(c), B6(d), B6(e), and B6(f). Interestingly, many of the processes listed are unlikely to lead to the formation of CH_3S radicals, e.g., B6(a), B6(b), B6(d), and B6(f).

Quite significant in the above list of reactions is process B6(f) involving the removal of CH_3SCH_2OOH by surface deposition and/or by wash-out and rain-out processes. In this case, surface deposition velocities of 0.5–1.5 cm s^{-1} would appear to be realistic and thus would define a pathway by which modified DMS was returned directly to the ocean. As shown in Figures 8.6(a) and 8.6(b), it is quite likely that many of the stable peroxides and intermediate acid species CH_3SOH and $CH_3S(O)OH$ would also have significant deposition rates to the ocean surface. If so, they potentially define a short circuit for DMS, preventing it from reaching the oxidized forms SO_2, SO_3, or MSA.

Concerning the chemistry of the CH_3S radical, recent kinetic studies of this species as well as the closely coupled CH_3SO_x species have produced several significant results but have also left many remaining unanswered questions. These have been summarized in the text below.

(a) The most likely reaction of CH_3S under remote MBL conditions is with O_3 to form CH_3SO and still other products not yet identified. Some of these "unidentified products" could in the final analysis turn out to be quite important. The reaction with O_2 to form equilibrated levels of CH_3SOO could also prove to be important. Of particular significance would be the yet unmeasured isomerization reaction involving the CH_3SOO species to give the non-peroxy form of this radical, CH_3SO_2.

(b) Considerable uncertainty still remains regarding the atmospheric fate of CH_3SO, although reactions with O_3 and O_2 are the most likely possibilities. In the first case the product formed under actual atmospheric conditions is unclear, but CH_3SO_2 is considered one of the more likely candidates. Other possibilities reported by Domine et al. (1992), such as CH_2SO, could also significantly alter the final product distribution. The product from the O_2 reaction should be $CH_3S(O)OO$, which, if reasonably stable, could totally dominate the chemistry of CH_3SO owing to the availability of high concentration levels of O_2.

(c) No kinetic studies have been reported involving the $CH_3S(O)OO$ radical, but the competitive processes C4(a) and C4(b) would seem to be the most likely

ones. The first reaction produces the radical intermediate CH_3SO_2, whereas, the second gives the potentially stable peroxide $CH_3S(O)OOH$. As in the case of the peroxy radical CH_3SOO, yet a third important reactive channel of the species $CH_3S(O)OO$ might involve its isomerization to form the radical intermediate CH_3SO_3, reaction C4(c).

(d) It has been speculated that the CH_3SO_2 radical is one of the single most important species leading to the formation of SO_2 via the thermal decomposition step C5(a). The most important competing step would likely be C5(b) involving reaction with O_2, giving the new peroxy radical $CH_3S(O)_2OO$. To the extent that reaction C5(b) dominates the chemistry of the sulfonyl radical (CH_3SO_2), very little SO_2 should be seen as a product. It is estimated that the C—S bond strength in CH_3SO_2 is approximately 20 kcal mol^{-1} (Turnipseed and Ravishankara, 1993), which means that reaction C5(a) has a very strong temperature dependence, shifting by nearly a factor of 2 for every 5 K change in temperature in the vicinity of 298 K.

(e) The kinetics of the peroxy radical $CH_3S(O)_2OO$ has not been studied, but it is expected to react in a fashion similar to the lower-oxidation-state peroxy species, except for reaction with O_2. In the latter case the sulfur in $CH_3S(O)_2OO$ is already hexavalent and therefore is unlikely to react further. The two major competing reactions, C6(a) and C6(b), lead to the CH_3SO_3 radical and the peroxide $CH_3S(O)_2OOH$, respectively.

(f) The CH_3SO_3 radical has been speculated to be a critical intermediate in the formation of the DMS oxidation products MSA(g) and H_2SO_4(g) (Bandy et al., 1992; Yin et al., 1990). The product MSA(g) would most likely form via reaction with HO_2 radicals, C7(a), whereas H_2SO_4(g) would be the product resulting from a two-step process, i.e., a thermal decomposition step, C7(b), to form SO_3 followed by the latter species' reaction with H_2O(g). As stated earlier in the text, a key aspect of the latter two-step process is that the H_2SO_4(g) formed by this reaction has the potential to form CCN in the atmosphere. As in the case of the sulfonyl radical, reaction C7(b) involves the breaking of an estimated 22 kcal mol^{-1} bond, meaning that the activation energy would be of at least this magnitude. Thus temperature changes of 5 K would again cause a potential shift in the product yield by a factor of 2. But, unlike the chemistry of the sulfonyl radical (CH_3SO_2), where it is speculated that reaction with O_2 is a major competing step to thermal decomposition, the sulfur in CH_3SO_3 is hexavalent and therefore should have a very low probability of reacting with O_2.

Conclusions: (1) To understand the product distribution from the oxidation of DMS will require a much more exhaustive examination of products that have been identified in studies to date. The most important of these are likely to be peroxide compounds. These range from the simple peroxide species generated from the parent compound, CH_3SCH_2OOH, to the more complex forms generated from the intermediate sulfur peroxy radicals, e.g., $CH_3S(O)_2OOH$. One

of the important characteristics of these peroxide products, as well as the intermediate acidic products CH_3SOH and $CH_3S(O)OH$, would be their tendency to undergo direct removal at the ocean surface via dry deposition or to be removed by wash-out or rain-out processes. In all three cases a direct short circuit would be provided for the return of DMS to the ocean surface without the formation of SO_2 or some form of sulfate. (2) The product distribution from DMS is most likely dependent on at least four critical factors: temperature, NO_x levels, HO_x levels, and surface deposition/wash-out rates. This suggests that the product distribution observed in field studies should be a strong function of geographical location, altitude, NO_x sources, MBL mixing times, time of day, and season of the year.

In general, temperature changes should influence the DMS product distribution in two ways: (a) in defining the relative branching in the reaction of OH with DMS into addition and abstraction channels, the abstraction channel being favored at temperatures above 285 K, and (b) in defining the relative importance of the unimolecular thermal decomposition steps C5(a) and C7(b) versus the competing bimolecular processes, i.e., C5(b), C5(c), and C7(a). Thus higher temperatures would seem to promote SO_2 and SO_3 formation.

Higher HO_x levels, on the other hand, would tend to increase the relative importance of OH versus NO_3 with respect to the DMS initiation reaction; and, within the abstraction pathway, higher HO_x levels would also have a strong influence on the relative yields of peroxide species versus SO_2 , SO_3, and MSA, i.e., the higher the HO_x level, the greater would be the yield of peroxides.

Higher levels of NO_x would influence the same processes as HO_x (e.g., the nature of the initiation reaction and the branching ratios for the reactions of several peroxy radical species), but these high levels would tend to have the opposite effect. For example, the importance of NO_3 versus OH as the initiating reactant would be promoted by elevated levels of NO_x; and, within the abstraction pathway, the production of SO_2, SO_3, and MSA would also be promoted relative to the peroxides.

Considering the strong interplay of the above variables, to assess the effect of temperature alone on the product distribution (a frequent topic of discussion in many reported field studies) must be considered very problematic. For example, within the MBL in the tropics the temperature tends to be high, HO_x levels are high, NO_x levels are very low, and MBL mixing is fast. At high latitudes, on average, temperatures are much lower, HO_x levels also tend to be lower, but NO_x levels are higher and mixing times tend to be somewhat longer. Thus one would speculate (based on Figures 8.6(a) and 8.6(b) and existing kinetic data) that at high latitudes the product distribution would reflect high yields of DMSO and possibly methanesulfinic acid and relatively lower yields of peroxides, SO_2, SO_3, and MSA. We note that both of the hypothesized major products are typically not measured in field studies. Still a further

complicating factor for the high-latitude analysis would be the possible importance of the NO_3 abstraction channel under night-time conditions. In the latter situation SO_2, SO_3, and MSA could be important products. In the tropics, on the other hand, one would speculate that the OH abstraction channel should be dominant, but high HO_x and low NO_x levels together with efficient mixing would tend to promote peroxide formation followed by surface loss. The oxidation products SO_3 and SO_2 as well as MSA might therefore be formed in somewhat lower yields. Again the only products typically measured in this type of setting have been SO_2 and aerosol phase MSA(p) and nss-SO_4^{2-}. Given such a scenario, any comparison of "measured" products between high latitudes and the tropics would appear to be meaningless in terms of the effects of only temperature as a controlling factor.

The above exercise, although highly speculative and qualitative in nature, does serve to point out that future progress in the elucidation of the DMS oxidation mechanism will require both further advances in field studies as well as detailed laboratory kinetic studies. Future field studies in particular need to move toward high-time-resolution measurements involving a much broader cross-section of both stable products and reactive intermediates.

CS_2 and OCS

The dominant sink for atmospheric CS_2 is reaction with OH in the troposphere (Chin and Davis, 1993). The reaction proceeds via reversible adduct formation,

TABLE 8.5(b) Tropospheric CS_2 Oxidation and Stratospheric Photochemistry of OCS: Important Mechanisms and Rate Constants

Reaction	Rate Constant[a,b]	Reference(s)
$OH + CS_2 + M \leftrightarrow CS_2OH + M$ $CS_2OH + O_2 \rightarrow$ products	$k_{eff} = \dfrac{1.25 \times 10^{-16}\exp(4550/T)}{T + 1.81 \times 10^{-3}\exp(3400/T)}$	1
$OCS + O \rightarrow CO + SO$	$1.6 \times 10^{-11}\exp(-2150/T)$	2
$OCS + h\nu \rightarrow CO + S$		
$S + O_2 \rightarrow SO + O$	2.1×10^{-12}[c]	2
$SO + O_2 \rightarrow SO_2 + O$	$1.4 \times 10^{-13}\exp(-2280/T)$	3, 4
$SO_2 + h\nu \rightarrow SO + O$		
$SO_2 + OH \xrightarrow{\text{multisteps}} H_2SO_4$ (see Table 8.5(c))		

[a] Units are cm^3 $molecule^{-1}$ s^{-1}.

[b] k_{eff} is the effective rate constant (at 760 Torr), defined as $k_{eff} = \dfrac{1}{[OH][CS_2]} \dfrac{d[product]}{dt}$.

[c] Independent of temperature.

1 Hynes et al. (1988), *J. Phys. Chem.*, **92**, 3846; 2 Atkinson et al. (1992), *J. Phys. Chem. Ref. Data*, **21**, 1125; 3 Black et al. (1982), *J. Chem. Phys. Lett.*, **93**, 598; 4 Goede and Schurath (1983), *Bull. Soc. Chim. Belg.*, **92**, 661.

probably of the SCS–OH isomer (Stickel et al., 1993a, and references therein), and further reaction of the adduct with oxygen. The effective rate constant, k_{eff}, for this mechanism is shown in Table 8.5(b). OCS, CO, and SO_2 have been observed as the corresponding products with yields of 0.83, 0.165, and 1.15, respectively (Stickel et al., 1993b). Based on these results, Chin and Davis (1993) estimated that the CS_2 + OH reaction generates about 30% of the total OCS in the atmosphere.

As mentioned earlier in the text (see Section 8.2 and Figure 8.4), OCS has a relatively long lifetime in the troposphere (4 years) where the reaction with OH represents the only important chemical sink, removing about 22% of OCS (Chin and Davis, 1993). Because it is sufficiently long-lived, it mixes into the stratosphere where the dominant loss processes are OCS photolysis and reaction with $O(^3P)$. Corresponding rate constants are given in Table 8.5(b). The atmospheric cycling of OCS and its potential relevance to global climate change are discussed in more detail in Section 8.4.3.

H_2S and SO_2

Figure 8.7 presents a schematic diagram of the mechanisms of H_2S and gas phase SO_2 oxidation in the atmosphere. Also included are estimates of characteristic times for the individual reactions based on room temperature and typical atmospheric concentrations of the reactants: $[OH] = 1 \times 10^6$, $[O_3] = 1 \times 10^{12}$, $[NO_2] = 2.5 \times 10^{10}$, and $[O_2] = 5 \times 10^{18}$, all in molecule cm^{-3} units. Corresponding reaction rate constants are summarized in Table 8.5(c). The kinetic scheme for oxidation of H_2S to SO_2 is reasonably well understood, primarily as a result of the work of Howard and co-workers (references 2 and 5–7, Table 8.5(c)). It is generally believed that the gas phase oxidation of SO_2 to H_2SO_4 involves four elementary steps. Key uncertainties remain in the rate of the $SO_3 + H_2O$ association reaction and in the rate of isomerization of $SO_3 \cdot H_2O$ to H_2SO_4; hence the generally accepted view that SO_3 is converted to H_2SO_4 with unit efficiency, while probably correct, should be looked upon with at least some degree of skepticism.

The mechanisms of aqueous phase absorption and oxidation of SO_2 have been extensively studied and reviewed (e.g., Martin, 1984). The processes involved represent the principal source of acidity in hydrosols in the remote atmosphere (and also in most of the polluted atmosphere). SO_2 dissolves in water according to the following equilibria:

$$SO_2(g) + H_2O \leftrightarrow SO_2 \cdot H_2O \tag{8.4}$$

$$SO_2 \cdot H_2O \leftrightarrow HSO_3^- + H^+ \tag{8.5}$$

$$HSO_3^- \leftrightarrow SO_3^{2-} + H^+ \tag{8.6}$$

The corresponding equilibrium constants are listed in Table 8.2. Simultaneous absorption of NH_3 significantly enhances SO_2 absorption due to its stabilizing (alkaline) effect on the pH of the hydrosol. Laboratory and field studies suggest that $SO_2(aq)$ (= $SO_2 \cdot H_2O + HSO_3^- + SO_3^{2-}$) is primarily oxidized by aqueous phase O_3 and H_2O_2. The reactions are first-order with respect to both $SO_2(aq)$ and $O_3(aq)$, and both $SO_2(aq)$ and $H_2O_2(aq)$ concentrations. The ozone oxidation reaction is strongly pH-dependent and dominates above approximately pH 5. In contrast, the reaction with H_2O_2 shows only a slight dependence on pH and dominates at low pH levels. Limited availability of oxidants or mass transport limitations in the gas/hydrosol system may reduce the rate of aqueous phase sulfuric acid formation.

In addition to the above processes, a major heterogeneous removal pathway for SO_2 in the MBL may be absorption and aqueous phase oxidation in alkaline sea salt particles. In a recent model study Chameides and Stelson (1992) have shown that the oxidation of $SO_2(aq)$ by $O_3(aq)$ in sea-salt at a typical pH of 8 proceeds sufficiently rapidly to explain nss-SO_4^{2-} levels measured in sea-salt

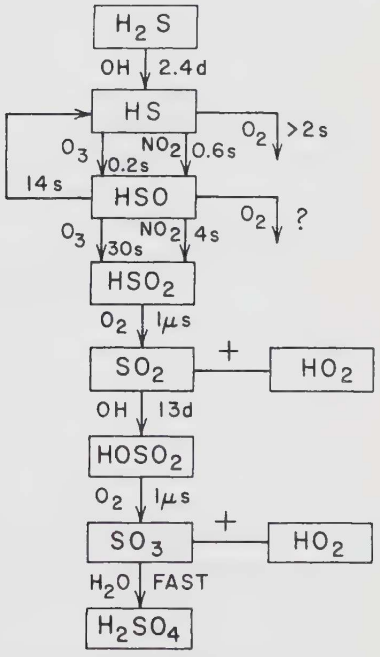


FIGURE 8.7. Major known steps in the atmospheric H_2S oxidation mechanism. Reactants and typical reaction lifetimes at room temperature are indicated next to the arrows. (Reproduced from Wang and Howard, 1990, reference 7, Table 8.5(c), with permission.)

TABLE 8.5(c) Rate Constants for the Atmospheric Photocemical Oxidation of H_2S and SO_2

Reaction	A[a]	E/R[b]	k(298 K)[a]	Reference(s)
$H_2S \rightarrow SO_2$				
$OH + H_2S \rightarrow SH + H_2O$	630	80	480	1
$NO_3 + H_2S \rightarrow SH + HNO_3$			<0.08	2
$Cl + H_2S \rightarrow SH + HCl$	3690	−210	7470	3
$SH + O_2 \rightarrow$ products			<0.00004	4
$SH + O_3 \rightarrow HSO + O_2$	950	280	370	1
$SH + NO_2 \rightarrow HSO + NO$	2600	−240	5800	4, 5
$HSO + O_2 \rightarrow$ products			<0.002	6
$HSO + O_3 \rightarrow SH + 2O_2$			7	7
$HSO + O_3 \rightarrow HSO_2 + O_2$			4	7
$HSO + NO_2 \rightarrow HSO_2 + NO$			960	6
$HSO_2 + O_2 \rightarrow HO_2 + SO_2$			30	6
$SO_2 \rightarrow H_2SO_4$				
$OH + SO_2 + M \rightarrow HOSO_2 + M$	40[c]	−260[c]	96[c]	1, 8
	10[d]	−470[d]	48[d]	1, 8
$HOSO_2 + O_2 \rightarrow HO_2 + SO_3$	1300	330	40	9
$SO_3 + H_2O + M \rightarrow SO_3 \cdot H_2O + M$			<0.6	10
$SO_3 \cdot H_2O + M \rightarrow H_2SO_4 + M$			[e]	

[a]Units are 10^{-14} cm^3 molecule^{-1} s^{-1} except where otherwise indicated.
[b]Units are degrees Kelvin.
[c]P = 760 Torr.
[d]P = 200 Torr.
[e]Generally assumed to be fast even though *ab initio* calculation (ref. 11) suggests a large barrier to isomerization.

1 Atkinson et al. (1992), *J. Phys. Chem. Ref. Data.*, **21**, 1125; 2 Dlugokencky and Howard (1988), *J. Phys. Chem.*, **92**, 1188; 3 Nicovich, Wang, and Wine (1994), *Int. J. Chem. Kinet.*, in press; 4 Stachnik and Molina (1987), *J. Phys. Chem.*, **91**, 4603; 5 Wang et al. (1987), *J. Phys. Chem.*, **91**, 5743; 6 Lovejoy et al. (1987), *J. Phys. Chem.*, **91**, 5749; 7 Wang and Howard (1990), *J. Phys. Chem.*, **94**, 8787; 8 Wine et al. (1984), *J. Phys. Chem.*, **88**, 2095; 9 Gleason and Howard (1988), *J. Phys. Chem.*, **92**, 3414; 10 Wang et al. (1989), *J. Chem. Phys.*, **89**, 4853; 11 Chen and Moore-Plummer (1985), *J. Phys. Chem.*, **89**, 3689.

particles over the North Atlantic. Their calculations further suggest that the bicarbonate/carbonate buffer system in sea-water and the flux of this alkalinity into the atmosphere largely control the removal of sulfur in the MBL (6–26 Tg SO_2 year^{-1}). They estimate that this sink is comparable to SO_2 removal by in-cloud oxidation and dry deposition in the MBL and is roughly comparable to the rate of DMS emission into the MBL. Therefore much of the SO_2 produced from DMS oxidation may be removed by sea-salt scavenging before having a chance to form new CCN particles in the atmosphere. Increasing anthropogenic

pollution of the MBL may, however, reduce the sulfur removal capacity of this natural cycle.

The relative importance, on a global scale, of gas and aqueous phase oxidation of SO_2 is still uncertain at this time. Some model calculations suggest that about 80–90% of the transformation of SO_2 takes place in the aqueous phase (e.g., Lelieveld and Heintzenberg, 1992). Corresponding lifetimes of SO_2 in the gas and aqueous phases are on the order of days to weeks and minutes to hours, respectively. However, the major aqueous phase oxidants, O_3 and H_2O_2, are predominantly supplied from the gas phase. Therefore oxidant availability can substantially control the overall efficiency of aqueous phase SO_2 oxidation.

8.3.2.2. The Polluted Atmosphere

In polluted air, metal-catalyzed oxidation by oxygen constitutes a significant additional pathway for the chemical removal of SO_2 in the aqueous phase. The transition metals Fe(+3), Mn(+2), and Cu(+2) are known to be strong catalysts, with Fe(+3) and Mn(+2) showing a synergistic effect on SO_2(aq) oxidation (Martin, 1984). The individual reaction rates are highly pH-dependent, and the reaction orders change with SO_2(aq) and metal concentrations. Carbon (soot) has also been found to catalyze the auto-oxidation of SO_2 adsorbed on the surface of soot particles, but this process appears to be limited by the available reactive surface area.

Aqueous phase absorption of SO_2 can be significantly hindered by a film-like accumulation of organic compounds in the surface layer of hydrosols. Furthermore, as mentioned in Section 8.2.2, the formation of relatively inert bisulfite–aldehyde addition compounds such as HMSA may efficiently reduce the production rate of H_2SO_4 in the aqueous phase. In addition, other organic compounds in solution, e.g., toluene, have been found to inhibit the catalytic oxidation of SO_2(aq) (Martin, 1984).

8.3.3. Deposition

Model studies generally assume that, on a global scale, atmospheric sulfur is cycled back to the Earth's surface mainly in the form of SO_2 and sulfate. Recent estimates of the corresponding dry and wet deposition fluxes for both compounds are summarized in Table 8.6. All studies listed in Table 8.6 have reported an approximate balance between total emission and deposition fluxes in the global atmospheric sulfur cycle. Assuming a balanced atmospheric sulfur budget, the global emission estimate given by the present authors (Table 8.4) – not including sea salt and soil dust contributions – is in relatively good agreement with the total sulfur deposition flux calculated by Langner and Rodhe (1991). Among the four studies listed in Table 8.6, the latter is the only one assuming a relatively low

TABLE 8.6 Global Sulfur Deposition Fluxes Estimated by Different Authors (Tg S year^{-1})

Region	Warneck (1988)	Bribmlecombe et al. (1989)	Langner and Rodhe (1991)[a]	Andreae and Jaeschke (1992)
Continents	71 (SO_2)[b]	33 (dry; SO_2: 17,		28 (SO_2; dry)
	42 (nss-SO_4)[c]	total SO_4: 16)		5 (total SO_4; dry)
	15 (sea-salt)	51 (wet; total S)		70 (total SO_4; wet)
			33 (SO_2; dry)	15 (sea-salt; dry + wet)
			19 (SO_2; wet)	
Oceans	15 (SO_2)	28 (dry; SO_2: 11,	7 (nss-SO_4; dry)	5 (SO_2; dry)
	28 (nss-SO_4)	total SO_4: 17)	38 (nss-SO_4; wet)	13 (nss-SO_4; dry)
	135 (sea-salt)	230 (wet; total S)		65 (nss-SO_4; wet)
				68 (sea-salt; dry)
				110 (sea-salt; wet)
Total	306	342	97[d]	379
	156[e]	178[d]		186[e]

"Dry" and "wet" refer to dry and wet deposition fluxes.

[a]Total (continental + oceanic) deposition fluxes.

[b]Dry deposition of SO_2 removes 50% of total S in urban and regionally polluted air.

[c]Includes 3 Tg S year^{-1} from oceans.

[d]Both sea-salt and soil dust fluxes excluded.

[e]Sea-salt flux excluded.

oceanic DMS emission rate (16 Tg S year^{-1}) which falls into the lower range of our corresponding estimate in Table 8.4. The Langner and Rodhe model also differs in its assumption of a relatively low anthropogenic SO_2 emission rate (67 Tg S year^{-1}). In summary, the major discrepancies among the individual studies listed in Table 8.4 arise from different estimates of oceanic DMS emissions, sulfur emissions from soils and plants, and anthropogenic sulfur emissions.

8.4. POSSIBLE IMPLICATIONS FOR GLOBAL CLIMATE CHANGE

8.4.1. DMS, Sulfate Aerosol, and Cloud Albedo

The role of clouds in the atmospheric radiation budget represents one of the largest uncertainties in predicting future climate change. As pointed out earlier (Sections 8.2.1 and 8.3.2.1), atmospheric sulfur chemistry is believed to be strongly linked to cloud formation via the production of CCN particles from condensable S(+6) species, predominantly H_2SO_4. Previous measurements

suggest that CCN particles consist mainly of sulfate and have a typical radius between 0.05 and 1.0 μm (e.g., Twomey,1971). Binary nucleation of sulfuric acid and water vapor (and possible co-nucleation of NH_3) initially yields low-nanometer-size sulfate particles (condensation nuclei; CN) which may grow into CCN by further condensation of these gases. The number density of CCN is closely related to the droplet size distribution of clouds which in turn has a significant effect on cloud albedo and therefore on global climate.

As our preceding discussion has shown, DMS emission by phytoplankton is believed to be the dominant source of sulfuric acid in the remote MBL. Recognizing the chemical link between DMS emissions and CCN production, Shaw (1983), followed by Charlson et al. (1987), proposed a hypothetical feedback mechanism involving an active thermostatic regulation of marine climate by DMS-producing algae. Specifically, it is assumed that warming of the atmosphere and surface oceans due to solar heat input or greenhouse gases would enhance the biological production of DMS and thereby its emission into the atmosphere. As a result, more CCN would be formed, increasing the cloud albedo and thereby producing a cooling effect which would counteract the assumed initial warming. For example, a 30% increase in CCN population over the oceans affecting only marine stratiform clouds would yield a change in the global heat balance of about $-1\,W\,m^{-2}$ (Charlson et al., 1987). This would significantly reduce the present global climate forcing from atmospheric CO_2 ($+1.5\,W\,m^{-2}$) and other greenhouse gases ($+0.95\,W\,m^{-2}$). Because about one-third of the Earth's surface is covered by oceanic stratus clouds, Charlson et al. (1987) proposed that this cloud-mediated effect of marine DMS emissions may have exerted a major forcing on global climate in pre-industrial times and that it still largely controls the present climate over remote marine regions.

The above hypothesis has been the subject of intense debate in the literature and, to this date, remains highly controversial. Notably, Schwartz (1988) posed a substantial test to the hypothesis based on the argument that anthropogenic SO_2, like DMS, also results in CCN formation in the atmosphere. He argued that despite the fact that sulfate levels in the northern hemisphere have been strongly enhanced due to man-made sulfur emissions, climatological records from the last 100 years have shown no significant differences in cloud albedo or mean surface temperature between the two hemispheres. Based on these data, he concluded that anthropogenic sulfur emissions and, by extension, marine DMS emissions have no significant effect on global cloud albedo.

However, in a lively response to Schwartz's paper, several authors have pointed out that such a clear conclusion cannot yet be drawn. One major argument is that the relationship between anthropogenic sulfur emissions and CCN number density is highly non-linear. Only a small fraction (*ca* 6%) of anthropogenic SO_2 contributes to form new CCN particles in the atmosphere, while typically 50% is removed via dry deposition (Table 8.6), mainly over the

continents. Most of the remainder becomes associated with pre-existing particles through in-cloud oxidation processes (Langner et al., 1992). On the other hand, oceanic DMS emissions represent a widely distributed source, and atmospheric DMS oxidation may significantly contribute to CCN formation in remote marine regions where the number of pre-existing CCN is low. Recent model calculations (Lin et al.,1992; Lin and Chameides, 1993) suggest that the degree of coupling between DMS emissions and CCN formation strongly depends on the mechanism by which sulfuric acid is produced from DMS oxidation. The results show that the production of new CCN should be negligible if SO_2 is the dominant intermediate in the DMS–H_2SO_4 pathway because of the efficient removal of SO_2 by alkaline sea-salt particles. However, if instead SO_3 is the major intermediate, as discussed earlier, the model predicts a significant CCN production rate of about 24 cm^{-3} day^{-1}.

The strongest evidence obtained to date for a DMS–CCN linkage are the results from long-term measurements of aerosol MSA (as tracer for DMS) and CCN concentrations at Cape Grim, Tasmania (Ayers and Gras, 1991). Both MSA(p) and CCN levels showed a strong annual variation with maximum values occurring during austral summer. A statistical evaluation of the data suggests a significant non-linear relationship between atmospheric DMS and CCN levels. In view of the complex chemistry of atmospheric DMS oxidation, it should be expected that the DMS–CCN linkage is non-linear. All the questions addressed in Section 8.3.2.1 must be answered before the role of DMS in global climate regulation can be quantitatively assessed. As per the discussion in Section 8.3.2.1, this requires detailed knowledge not only of reaction rate constants pertinent to atmospheric DMS oxidation but also of the relative yields of intermediate products and end-products resulting from this oxidation. In addition, the physical processes involved in CCN formation also contribute to this non-linearity. As mentioned earlier, the yield of new particles due to homogeneous nucleation of H_2SO_4 (and possibly MSA(g)) is inversely related to the number of already produced or pre-existing particles based on the total surface area available for heterogeneous condensation. Additional processes contributing to the above non-linearity may involve cloud-mediated CCN formation, i.e., the presence of clouds may have a "self-promoting" effect by enhancing the production of CCN (Saxena and Grovenstein, 1993; Hegg et al., 1990). It has been suggested that aqueous phase oxidation of SO_2 in cloud-water followed by evaporation of cloud droplets modifies the aerosol size distribution and chemical composition in a given air mass such that the resulting particles are ideally suited for activation as CCN. Thus relatively more particles may be activated as CCN at a given supersaturation in air which has been processed through clouds. In addition, the supersaturation field itself may be altered in favor of CCN formation. Such mechanisms could explain previous observations of elevated CCN levels in the vicinity of clouds.

The data obtained at Cape Grim are consistent with a climate-stabilizing feedback loop as proposed in the DMS–cloud–climate hypothesis. However, measurements of MSA and nss-SO_4^{2-} in the Vostok ice core (Antarctica) covering the last glacial/interglacial cycle back to 160,000 years have provided evidence apparently in direct conflict with this view (Legrand et al., 1991). Elevated levels of both compounds were found for the period near the end of the last ice age suggesting an increase in oceanic DMS emissions and thus an amplifying rather than stabilizing effect on climate change. It is possible that the observed increase resulted from a shift in favor of DMS-producing biota in the surrounding ocean. On the other hand, changes in aerosol-scavenging processes and/or snow accumulation rates may have also contributed to the observed pattern.

As the previous discussion has shown, large uncertainties still remain in estimating the effects of marine DMS and anthropogenic SO_2 emissions on cloud albedo and global climate. At this time, not even the sign of the proposed DMS–cloud–climate feedback is known (amplification, stabilization, or no regulation of climate). Basically, the response of the DMS-producing system in seawater to changes in climate factors such as temperature and UV radiation are unknown. Overall, the relative importance of DMS versus anthropogenic SO_2 emissions with respect to cloud albedo over the oceans is difficult to estimate because of the many non-linear processes involved. However, recent satellite measurements over the central North Atlantic showed a correlation between chlorophyll concentration, sea surface temperature, and cloud albedo suggesting a predominantly marine source of CCN (Falkowski et al., 1992). By comparison, effects of anthropogenic sulfur emissions from the eastern United States on marine cloud albedo were only detectable in the immediate vicinity of the US coast. In future field programs such measurements should be combined, e.g., with studies of sulfur isotope ratios in marine aerosol to obtain a more quantitative estimate of the source strength and climatic role of biogenic sulfur over the oceans.

More studies are also needed to understand the impact of anthropogenic sulfur emissions on cloud albedo over land. Recently Leaitch et al. [1992] reported measurements made over eastern North America since 1982 indicating a significant enhancement of cloud droplet number concentrations by anthropogenic sulfur pollution. They estimated a corresponding climate forcing of -2 to $-3\ W\ m^{-2}$ for this region. On a global average the cloud albedo forcing by anthropogenic sulfate may be on the order of $-1\ W\ m^{-2}$ (Charlson et al., 1992), most of which is confined to the NH, with large geographical and seasonal variations. However, it should be kept in mind that such estimates are rather crude, mainly because the mass concentration of atmospheric sulfate does not linearly translate into cloud droplet number concentration, which in turn may not be linearly related to cloud albedo.

8.4.2. Radiative Backscattering by Tropospheric Sulfate Aerosol

Much of the subject of the following two sections has already been discussed in Chapter 5, so only a brief overview will be given here. Detailed models have been developed in recent years to estimate the direct climate forcing of sulfur emissions, i.e., the effect of backscattering of short-wave solar radiation by sulfate aerosol. Based on three-dimensional numerical calculations, Charlson et al. (1991) established a global distribution map of the aerosol sulfate mass concentration in the troposphere. The source terms in the model included both anthropogenic and natural sulfur emissions. Using this map and an empirically derived expression for the optical depth of sulfate aerosol, they inferred a global distribution of the backscatter flux of solar radiation from tropospheric sulfate. The results suggest a global average radiative forcing of about $-1\ W\ m^{-2}$, similar but opposite in sign to the present-day greenhouse effect of CO_2 ($+1.5\ W\ m^{-2}$). A subsequent study by Lelieveld and Heintzenberg (1992) showed that much of the direct aerosol forcing may be due to cloud processing of air effecting a shift in the size distribution of sulfate particles (see previous section). The sulfate aerosol resulting from evaporating clouds occurs predominantly in a size range which scatters solar radiation much more efficiently than particles produced through gas phase oxidation of SO_2. More recently Kiehl and Briegleb (1993) recalculated the global climate forcing of sulfate aerosols using more refined assumptions for the optical parameters in their model compared with the model by Charlson et al. (1991). Their results suggest a direct forcing of $-0.54\ W\ m^{-2}$ on a global average and mean values of -0.72 and $-0.38\ W\ m^{-2}$ for the NH and SH, respectively. The relative contribution of anthropogenic versus natural sulfate to this forcing is estimated to be 52% globally, 60% in the NH, and 34% in the SH.

In summary, it appears that the cooling effect of tropospheric sulfate aerosol is dominated by anthropogenic sources over the continents and by natural sources over the oceans. The sum of the direct and indirect (cloud albedo) cooling by sulfate seems to be large enough to significantly offset the total warming from greenhouse gases ($+2.1$ to $+2.5\ W\ m^{-2}$), at least over the highly industrialized regions of the NH. Net greenhouse warming may therefore only occur as a patchy phenomenon, with large geographical and seasonal variations.

8.4.3. The Stratospheric Sulfate (or "Junge") Layer

Relatively little is known at the present time about the potential climate forcing due to changes in the stratospheric sulfate burden. The stratospheric sulfate layer, first discovered by C. Junge in the late 1950s (Junge et al.,1961),

envelopes the entire globe and its maximum density occurs at roughly the same altitude (15–23 km) as the stratospheric ozone density maximum. During volcanic quiescent periods and under normal mid-latitude stratospheric conditions (say, 20 km altitude and 220 K temperature) the sulfate aerosol has a number density of some 10 particles cm^{-3}. The particles have an average radius of 0.07 μm and a composition of about 75% H_2SO_4 and 25% H_2O. Crutzen (1976) suggested that the presence of the stratospheric "background" aerosol may be mainly due to OCS photolysis. Many authors have since then discussed the potential for a global climate cooling trend due to increasing OCS levels (see the review by Chin and Davis, 1993, and references therein). However, as discussed earlier in Section 8.2.2, there is no clear evidence to this date that atmospheric OCS levels have actually increased since their earliest measurements in the 1970s. As mentioned earlier, a recent model study by Chin and Davis (1995) has shown that the lifetime of OCS in the stratosphere is about 10 years, or more than two times longer than its total atmospheric lifetime. The model further predicts that most OCS transported into the stratosphere (91%) returns to the troposphere. About 71% of the tropospheric OCS is removed by vegetation and 22% by reaction with OH. Thus previous studies may have largely overestimated the production rate of stratospheric sulfate from OCS and may have underestimated the influence of volcanic eruptions on the stratospheric "background" aerosol.

Powerful volcanic eruptions such as that of Mount Pinatubo in June 1991 can significantly enhance the sulfate particle density in the stratosphere over several years. Since these particles more effectively reflect short-wave solar radiation than they attenuate terrestrial long-wave radiation, the net result of such an event is cooling of the Earth's surface in affected regions. Recent satellite measurements of the radiative effects of the Pinatubo plume (Minnis et al., 1993) unambiguously showed a strong negative forcing (cooling) with an initial latitudinal maximum of $-10\ W\ m^{-2}$ near the equator. Such eruptions may also significantly perturb stratospheric ozone chemistry due to the enhanced surface area supplied by the resulting sulfate aerosols, potentially inducing a higher catalytic destruction rate of ozone. Other linkages between stratospheric ozone chemistry and the atmospheric sulfur cycle may also be important. For example, an enhancement of UV-B radiation at the Earth's surface due to lower stratospheric ozone levels may reduce the population of DMS-producing algae and at the same time increase oceanic emissions of OCS produced by photochemical processes in surface seawater. As we have already pointed out at the beginning of this chapter, scientists are only now beginning to understand the coupling of the atmospheric sulfur cycle to cycles of other elements in the atmosphere and to other earth reservoirs. The need for broad-based interdisciplinary research is obvious in order to find some answers to the many urgent questions outlined above.

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